$L1_0$ FePt thin films with [001] crystalline growth fabricated by ZnO addition and rapid thermal annealing

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FePt films with a high degree of order S of the $L1_0$ structure ($S > 0.90$) and well defined [001] crystalline growth perpendicular to the film plane are fabricated on thermally oxidized Si substrates by the addition of ZnO and a successive rapid thermal annealing (RTA) process. The optimum condition to prepare high-ordering $L1_0$ FePtZnO films is 20 vol% ZnO addition and 450 °C annealing. The effect of the ZnO additive on the ordering process of the $L1_0$ FePtZnO films is discussed. In the annealing process, Zn atoms move to the film surface and evaporate. The motion of the Zn atoms accelerates the intergrain exchange and decreases the ordering temperature.

Keywords: FePt thin film, magnetic recording material, rapid-thermal-annealing, oxide addition

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1. Introduction

The FePt intermetallic alloy with an $L1_0$ ordered structure is considered as one of the leading candidate materials for the next generation of ultrahigh-density magnetic recording media because of its large magnetocrystalline anisotropy constant (7×10^7 erg/cm^3, 1 erg = 10^{-7} J), small grain size (about 3 nm) permitting thermal stability, high coercivity, and excellent corrosion resistance.[1] One of the key challenges of the application of FePt films with $L1_0$ structures for perpendicular magnetic recording media is to control the c-axis textures of the films. Usually, FePt films deposited on glass or oxidized Si substrates tend to grow in a random orientation or into (111) textures along the c axis of the grain at 37° with respect to the film plane.[2,3] For perpendicular recording application, the orientation of the $L1_0$ FePt film should have the c-axis perpendicular to the film plane. Many efforts, such as doping[4,5] and using an underlayer,[6] single-crystal MgO (001) substrates,[7] nonepitaxial growth,[8,9] etc, have been made to use the $L1$ FePt (001) texture as a perpendicular magnetic recording medium. In recent years, bit patterned media (BPMs) have attracted increasing attention because they are a possible approach to overcoming the onset of superparamagnetism and consequently increasing the areal recording density of the hard disk drive.[10,11] Although some studies have successfully been conducted on FePt BPM samples,[12,13] several challenges remain, such as the realization of smaller dot sizes, better perpendicular orientation of the c axis, lower thermal annealing temperature, and the non-epitaxial growth method. In this study, we prepare $L1_0$ FePt thin films with a high degree of order S of the $L1_0$ structure ($S > 0.90$) and well defined [001] crystalline growth perpendicular to the film plane for BPM.

It has been demonstrated that the alternate monatomic layer deposition of Fe and Pt is a very effective method of preparing $L1_0$ FePt film with excellent (001) orientation and perpendicular magnetic anisotropy at low annealing or deposition temperature.[14,15] It was also reported that the oxide addition-rapid thermal annealing (OA-RTA) process is effective in preparing $L1_0$ FePt films with (001) orientation and perpendicular magnetic anisotropy and in lowering the annealing temperature.[16,17] We chose a proper oxide as an additive to Fe and Pt alternate monatomic layers, enhancing the ordering parameter and lowering the ordering temperature. The addition of metals with high diffusion constant will activate interatomic diffusion in films. The diffusion constant relates to the melting point. Therefore, oxide additives containing metals that have low melting points are expected to lower the ordering temperature of $L1_0$ FePt films. Considering the melting point of the metal and the free energy of the formation of oxide, ZnO is chosen as an additive to prepare FePt films in order to further increase the degree of order and lower the annealing temperature.

2. Experiment

$[Fe/Pt/ZnO]_{18}$ films were deposited in a multilayer sputter system on thermally oxidized Si substrates at ambient temperature. The thickness values of the Fe and Pt layer in the multilayers were kept at 0.22 nm and 0.18 nm, respectively. The

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thickness of each ZnO layer varied from 0 nm to 0.12 nm, and the ZnO addition amounted to about 0 vol%–30 vol% of the sum of the single Fe and Pt layer thickness. The base pressure of the deposition chamber was about 3×10^{-5} Pa and Ar gas was kept at a pressure of 0.5 Pa during sputtering. The substrates were rotated during film deposition to obtain uniform films.

After deposition, the films were annealed using a rapid-thermal-annealing (RTA) system. RTA was performed under a vacuum of $\sim 10^{-4}$ Pa. The heating rate was 60 °C/s, the annealing temperature was in a range of 350 °C–600 °C, and the films were kept at these temperatures for 10 min. The crystal structures of the films were characterized by θ–2θ scan X-ray diffraction (XRD) with Cu K_α radiation and transmission electron microscopy (TEM). The composition analysis along the depth direction was performed with a photoelectric spectrum device (XPS), and the magnetic properties were measured by a vibrating sample magnetometer (VSM). The surface morphologies and magnetic domain structures of the samples were investigated using atomic force microscopy (AFM) and magnetic force microscopy (MFM).

3. Results and discussion

Figure 1(a) shows the XRD results of the $[Fe/Pt/ZnO]_{18}$ films with the ZnO addition amount increasing from 0 to 30 vol%, annealed at 450 °C for 10 min. The XRD pattern of the film without ZnO addition shows FePt (001), (002), and (111) peaks, which indicates that this film does not have perfect [001] crystalline growth perpendicular to the film plane. The XRD patterns of the films with ZnO additive varying from 5 vol% to 30 vol% show only FePt (001) and (002) peaks but no FePt (111) peak, which means that all these films are of [001] crystalline growth. Figure 1(b) shows the relationship between the ZnO addition amount and full width at half maximum (FWHM) of the (001) peaks obtained by rocking curve measurement. We have a minimum FWHM when the ZnO addition amount is 20 vol%, which indicates the highest degree of $L1_0$ ordering. Similar results can be obtained when the annealing temperature is 400 °C and 500 °C. So we have the addition of ZnO enhanced $L1_0$ ordering, and the optimum addition amount is 20 vol%.

After we have obtained the optimum addition amount of the ZnO additive, our study focuses on the $[Fe/Pt/ZnO]_{18}$ (ZnO 20 vol%) films. Figure 2 shows the XRD patterns of the $[Fe/Pt/ZnO]_{18}$ (ZnO 20 vol%) film samples annealed at 350 °C–600 °C for 10 min. All the XRD patterns show (001) and (002) diffraction peaks, and there is almost no (111) peak. This means that we can obtain the $L1_0$ ordered FePt films even when the annealing temperature is as low as 350 °C. It was reported that the initial ordering temperature of the $[Fe/Pt]_n$ multilayers was higher than 350 °C.[15] Our results show that the initial ordering temperature of the $[Fe/Pt/ZnO]_{18}$ multilayers is lower than 350 °C. This means that the ZnO addition can lower the ordering temperature of the $[Fe/Pt]_{18}$ multilayers.

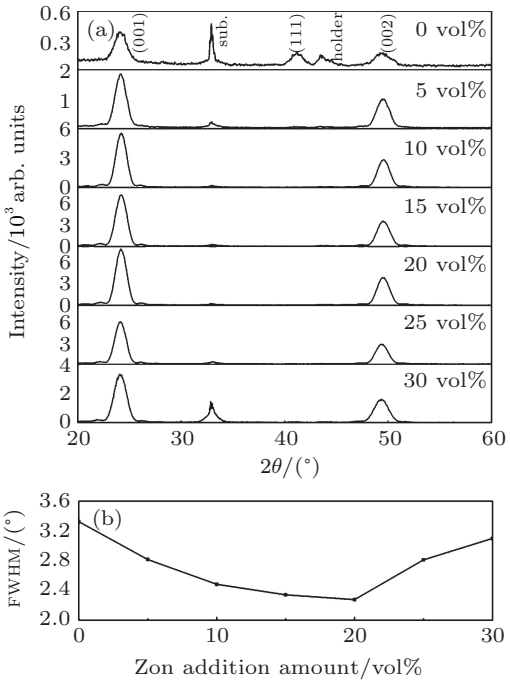


Fig. 1. (a) The XRD patterns of $[Fe/Pt/ZnO]_{18}$ films, with the ZnO addition amount increasing from 0 vol% to 30 vol%, annealed at 450 °C for 10 min. (b) The relationship between the ZnO addition amount and the FWHM of the (001) peak, obtained by rocking curve measurement.

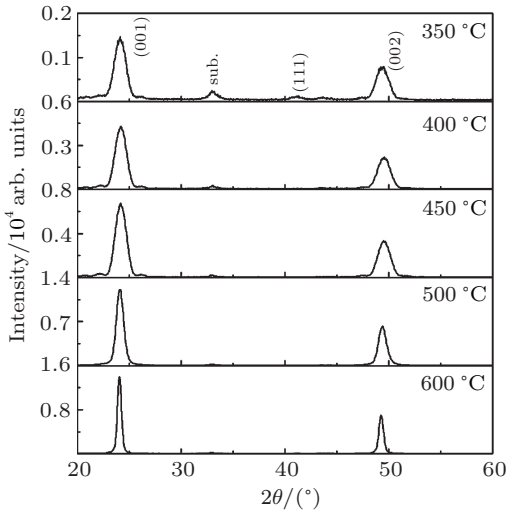


Fig. 2. The XRD patterns of the $[Fe/Pt/ZnO]_{18}$ (ZnO 20 vol%) film samples annealed at 350 °C–600 °C for 10 min.

The order–disorder transformation of the FePt phase involves a distortion of the fcc unit cell. The lattice constant a expands approximately 2%, while the lattice constant c contracts approximately 2.5%, resulting in a c/a ratio of less than 1. The ordering parameter S of the FePt film relates to the lattice constant, and the heating temperature in the RTA process strongly affects the quality of the film. To further study the effect of ZnO addition in the ordering process of the FePt films, the film structure is analyzed by fitting the XRD (θ–2θ scan) profiles to the out-of-plane measurements. In general,

the X-ray intensity scattered from a thin film, which is stacked by n-unit cells with a lattice constant d, is calculated from

$$I(Q) = \int L(Q)|F(Q)|^2 L_{\rm p}\, {\rm e}^{-2M} \frac{1}{1+k^2(Q-q)^2}\, {\rm d}q, \qquad (1)$$

where $L(Q)$ is the Laue function, $F(Q)$ the structure factor, $L_{\rm p}$ the polarization factor, ${\rm e}^{-2M}$ the temperature factor, k the device correction, and $Q = 4\pi \sin\theta/\lambda$. In this research, the degrees of chemical order and crystalline orientation are evaluated by considering structural disorders such as the distribution of the chemical order and the fluctuation of the lattice constant in Eq. (1). The degree of chemical order S is determined by fitting the out-of-plane profile of the FePt ($00m$) ($m = 1$, 2, 3, and 4) peaks. The atomic scattering factor f_{hkl} (hkl = 001 and 002) for each atomic plane is calculated by the following equation

$$f_{hkl} = \{(1 \pm S) f_{\rm Fe} + (1 \mp S) f_{\rm Pt}\}/2. \qquad (2)$$

Here, $f_{\rm Fe}$ and $f_{\rm Pt}$ are the atomic scattering factors of Fe and Pt, respectively. In this case, FePt film is continuously transformed from a disordered phase to an ordered phase. The details of the calculation model and the fitting procedure are given elsewhere.[18] Figure 3 shows the ordering parameter S and the c/a ratio of the FePt films, each as a function of the annealing temperature. With the increase in annealing temperature, the ordering parameter S increases and reaches a maximum of 0.92 at 450 °C, and the c/a ratio decreases and drops off to a minimum. These results indicate that the fcc-to-fct phase transition is complete when the samples are annealed at 450 °C. So we can discover that a 20 vol% ZnO addition and 450 °C annealing temperature are the optimum conditions to prepare high-ordering $L1_0$ FePt films.

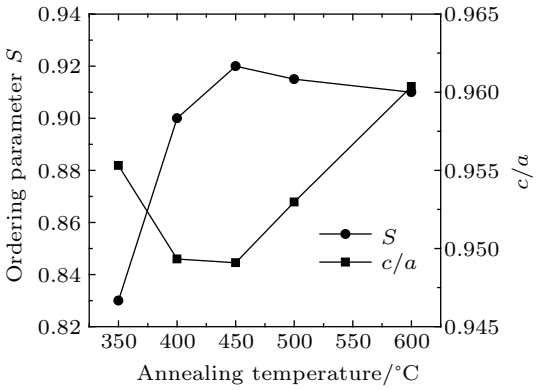


Fig. 3. The dependences of the ordering parameter S and the c/a ratio of the FePt films on the annealing temperature.

Figure 4 shows the AFM and MFM images of the FePt films with and without ZnO addition, annealed at 450 °C for 10 min. The films are not magnetized by VSM or other equipment. The magnetic FePt tip is magnetized by VSM along the pinpoint direction before being measured. The scan size of all the images is 3 μm × 3 μm. A remarkable change in the surface morphology of the film is observed in the figure. The morphology of the $[{\rm Fe/Pt}]_{18}$ film annealed at 450 °C appears to be many isolated particles embedded in continuous film, and the morphology of the $[{\rm Fe/Pt/ZnO}]_{18}$ (ZnO 20 vol%) film annealed at 450 °C presents a very flat continuous surface. The values of surface roughness Ra are 0.4 nm and 0.3 nm for the above two films, respectively. Our group reported on the mechanism of the $L1_0$ FePt thin-film grain growth with the increase in annealing temperature.[19] Because of the in-plane tensile stress, two-dimensional grain growth occurs first at a lower annealing temperature, and the particulate FePt film is finally formed with the further increase in annealing temperature. For the flat continuous films, we believe that $[{\rm Fe/Pt/ZnO}]_{18}$ (ZnO 20 vol%) film annealed at 450 °C is composed of two-dimensional $L1_0$ FePt grains in the film plain. We suppose that Zn atoms accelerate the exchange of Fe and Pt atoms in the annealing process, so we can obtain a very flat continuous surface and high degree of order S at lower annealing temperature. The MFM images are characterized by adjacent bright or dark spots which imply that their corresponding magnetic moments are upward or downward, respectively. The MFM image of the $[{\rm Fe/Pt}]_{18}$ film annealed at 450 °C shows a smaller magnetic domain size, which means a weak exchange–coupling interaction among the magnetic grains. This can be seen from the corresponding AFM images of the film, where some isolated particles are embedded in continuous film, which could reduce the exchange coupling interaction among the magnetic grains. With the addition of ZnO, the magnetic domain sizes increase, which means that the exchange–coupling interaction among the magnetic grains becomes strong. ZnO addition leads to an increase in the grain size, and the film has a continuous structure with strong exchange–coupling interaction among the magnetic grains, as shown in the corresponding AFM image.

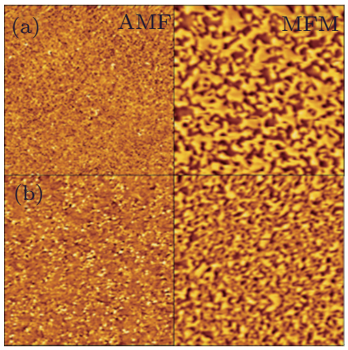


Fig. 4. (color online) AFM and MFM images (3 μm × 3 μm) of (a) $[{\rm Fe/Pt/ZnO}]_{18}$ and (b) $[{\rm Fe/Pt}]_{18}$ film annealed at 450 °C for 10 min.

To further study the ZnO effects in the ordering process, the composition analysis of the $[{\rm Fe/Pt/ZnO}]_{18}$ (ZnO 20 vol%) film along the depth direction is performed with a photoelectric spectrum device (XPS), as shown in Fig. 5. From Fig. 5(a),

we can find that Zn atoms can be detected in the as-deposited $[Fe/Pt/ZnO]_{18}$ (ZnO 20 vol%) film, and from Fig. 5(b) we can find that no Zn atoms are detected in the $[Fe/Pt/ZnO]_{18}$ (ZnO 20 vol%) film with annealing process. This means that Zn atoms move to the surface of the film and evaporate in the annealing process. The motion of Zn atoms accelerates the exchange of Fe and Pt atoms and reduces the ordering temperature. From the images we can see that the Fe atom content is higher than the Pt atom content. According to the layer structure given in the experimental section, the Fe-to-Pt atomic ratio is approximately 0.62:0.38. But TEM-EDS measurements show that the Fe-to-Pt atomic ratio is about 1:1 in the FePt grains and an Fe–O compound exists in the grain boundary. From Fig. 5(b) it follows that the oxygen content is relatively high, which is caused by the Fe–O compound.

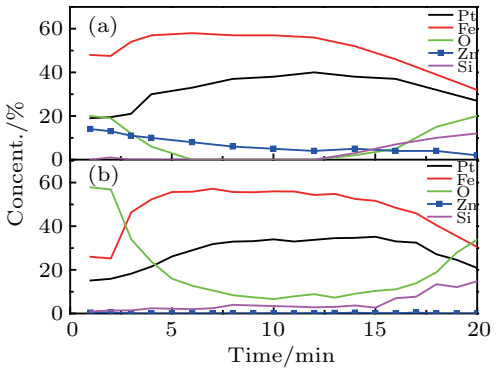


Fig. 5. (color online) The XPS results of the $[Fe/Pt/ZnO]_{18}$ (ZnO 20 vol%) films (a) without annealing and (b) with annealing at 450 °C.

Figure 6 shows the plan view TEM and HRTEM images of the $[Fe/Pt/ZnO]_{18}$ (ZnO 20 vol%) film annealed at 450 °C. From the TEM images we can see that the film is composed of two-dimensional FePt grains grown in the film plain. The average grain size is more than 100 nm in the film plane direction. From the HRTEM results we can find that the FePt grains have a high degree of order of the $L1_0$ structure and well-defined [001] crystalline growth perpendicular to the film plane. Figure 7 shows the in-plane and the out-of-plane hysteresis loops

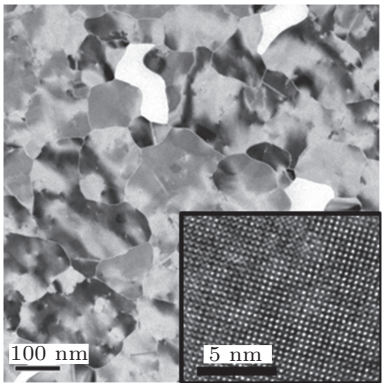


Fig. 6. TEM and HRTEM image of the $[Fe/Pt/ZnO]_{18}$ (ZnO 20 vol%) film annealed at 450 °C.

of the $[Fe/Pt/ZnO]_{18}$ (ZnO 20 vol%) film annealed at 450 °C for 10 min. The out-of-plane coercivity value is about 10 kOe (1 Oe = 79.5775 $A \cdot m^{-1}$) and the in-plane coercivity value is about zero. These results accord with the XRD and TEM results, and the FePt films are of well-defined [001] crystalline growth perpendicular to the film plane. They are suitable for BPM usage because of their excellent structural properties, lower thermal annealing temperature, and non-epitaxial growth method.

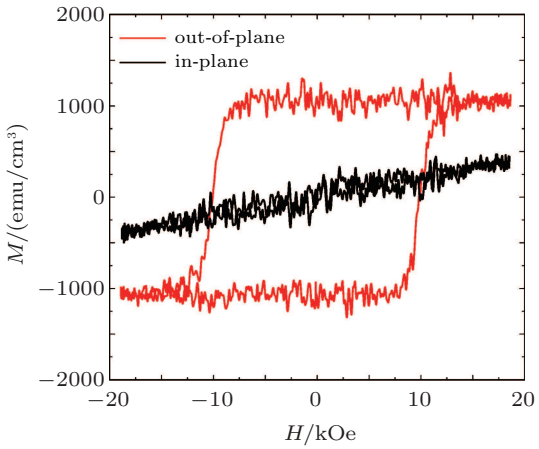


Fig. 7. (color online) The hysteresis loops of the [Fe/Pt/ZnO]18 (ZnO 20 vol%) film annealed at 450 °C for 10 min.

4. Conclusions

FePt films with a high degree of order S of the $L1_0$ structure ($S > 0.90$) and well defined [001] crystalline growth perpendicular to the film plane are fabricated on thermally oxidized Si substrates by the addition of ZnO and a successive rapid thermal annealing process. The optimum condition for preparing high-ordering $L1_0$ FePt films is 20 vol% ZnO addition and a 450 °C annealing temperature. The Zn atoms move to the surface of the film and evaporate in the annealing process, and the motion of the Zn atoms accelerates the exchange of Fe and Pt atoms and reduces the ordering temperature. This FePt film is suitable for BPM use.

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