

Early Stage Growth Structure and Stress Relaxation of CoCrPt Thin Films on Spherically Modulated Polymer Surface

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(Received 16 February 2010, Received in final form 10 March 2010, Accepted 12 March 2010)

Combined study of *in-situ* stress measurements and atomic force microscopy (AFM) revealed drastic stress relaxation in the CoCrPt and PS(styrene)-PVP(vinyl pyridine) polymer hybrid structure that was closely related to the growth structure of the film. We have observed not only no large initial growth stress at the initial stages of film growth but also twice smaller stress in magnitude with opposite sign in the CoCrPt/PS-PVP/Si sample. The microstructural studies using AFM at the various film growth stages revealed that the film growth structure plays an important role in the stress relaxation mechanism of CoCrPt films on a corrugated polymer surface.

Keywords : stress, CoCrPt, interface, diblock copolymer

1. Introduction

Recent studies have focused on artificially roughened surfaces because it may be possible to provide a well-defined rough surface/interface and obtain desirable magnetic properties by artificially creating and controlling the surface structure and morphology [1-3]. For example, McMichael *et al.* used obliquely sputtered Ta underlayers to generate large anisotropy fields in normally deposited ultrathin NiFe and Co films, whereas Jiang *et al.* examined the interdependence between the structural roughness parameters and magnetic properties of ultrathin Co films grown on smooth and rough Cu(001) substrates [4, 5]. Theoretically, Zhao *et al.* examined the influence of the surface/interface roughness on the demagnetizing factor of a thin magnetic film with a single or double boundary of self-affine, mound, or anisotropic roughness [6]. They confirmed the strong dependence of surface magnetization on the surface roughness as well as the effects of the surface roughness on the magnetic domain wall thickness, domain size, and coercivity of thin magnetic films. Quite

recently, an ion sculpting technique was used to investigate the step-induced in-plane uniaxial magnetic anisotropy and spin reorientation transition [7, 8]. In our previous work, we introduced a spherically modulated polymer surface to examine the effect of roughness on perpendicular magnetic anisotropy [9]. However, the origin of the changes in magnetic anisotropy energy due to the introduction of a modulated surface is unclear.

A diblock copolymer template, in which a microphase separates into a monolayer of domains, is one of the most promising candidates for nanoscale patterning that is otherwise impossible by lithographic procedures [10, 11]. Diblock copolymers, which consist of two chemically distinct polymer segments bonded covalently together, can form ordered periodic arrays of spheres, cylinders, or lamellae depending on the volume fraction of the component. The size and type of ordering can be controlled by changing the molecular weight, chemical structure, molecular architecture and composition of the block copolymers. This results in a periodically modulated morphology typically with domains of periodicity in the 10-100 nm range [12]. This study examined the correlation between mechanical stress and the growth structures of Co₆₈-Cr₁₈Pt₁₄ thin films deposited on a periodically-modulated,

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PS₂₁₄₀₀(styrene)-PVP₂₀₇₀₀(vinyl pyridine) diblock copolymer with a self-assembled surface.

2. Experimental

CoCrPt films were prepared at ambient temperature by dc magnetron sputtering under a base pressure of 8×10^{-7} Torr and an Ar sputtering pressure of 3 mTorr. The typical deposition rate, which was obtained under an applied power of 150 W to each target and a substrate-to-target distance of 50 mm, was 1.9 Å/s. A Si(100) substrate was cleaned first in a $\text{NH}_4\text{OH}:\text{H}_2\text{O}:\text{H}_2\text{O}_2=1:5:1$ (v:v:v) solution at 80°C for 15 minutes followed by rinsing with Milli-Q water (>18 mW). The diblock copolymer PS₂₁₄₀₀-PVP₂₀₇₀₀ ($N_{\text{PS}}-N_{\text{PVP}}=205-200$) was purchased from Polymer Source Inc. and dissolved in toluene, which is a good solvent for a PS block, and a non-solvent for the PVP block. It forms a spherical micelle, 49 nm in diameter, which was measured by Dynamic Light Scattering (DLS). In a toluene solution, the core of the 3-dimensional micelle is composed of a PVP block, whereas the PS chains form a corona. The critical micelle concentration (CMC) and aggregation number, as determined by DLS, was 0.7 mg/ml and 6 (chains per micelle), respectively [13, 14]. Cleaned Si substrates were immersed in a 10 mg/ml PS₂₁₄₀₀-PVP₂₀₇₀₀ (in toluene) solution for 20 seconds, and then rinsed in pure toluene for 5 seconds to remove any weakly attached residue. Atomic force microscopy (AFM) topography images showed that the peak-to-peak distance ($D_{\text{peak-to-peak}}$) and height (h) of the ordered micelles was 407 nm and 2.4 nm, respectively. In these measurements, noncontact mode AFM (PSI Autoprobes CP) and a Si_3N_4 tip with a spring constant 3.2 N/m was used. Growth stress of CoCrPt films were measured using an *in-situ* high-sensitive laser deflection system with a 1-dimensional position sensitive detector (PSD), as shown in Fig.

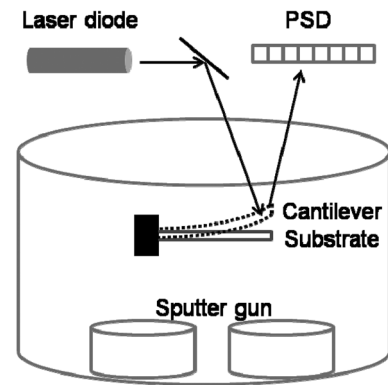


Fig. 1. Schematic diagram of the *in-situ* stress measurement system.

1. Details of the measurement system are reported elsewhere [15, 16]. The level of growth stress was determined from the change in curvature (R) of the substrate using the following equations [17]:

$$\sigma = \frac{Y_s t_s^s}{6(1 - \nu_s^2) t_f} \frac{1}{R} \quad (1)$$

where Y_s , ν_s , and t_s are Young's modulus, Poisson's ratio, and substrate thickness, respectively, and t_f is the film thickness.

3. Results and Discussion

Fig. 2 shows the evolution of the force/width curve of the CoCrPt/Si and CoCrPt/PS-PVP/Si samples, respectively, which was measured using an *in-situ* stress measurement system. The positive and negative slope in Fig. 2 means tensile stress and compressive stress in the film, respectively. It should be noted that the magnitude and sign of the stress observed in the CoCrPt/Si and CoCrPt/PS-PVP/Si samples are completely different. In the case

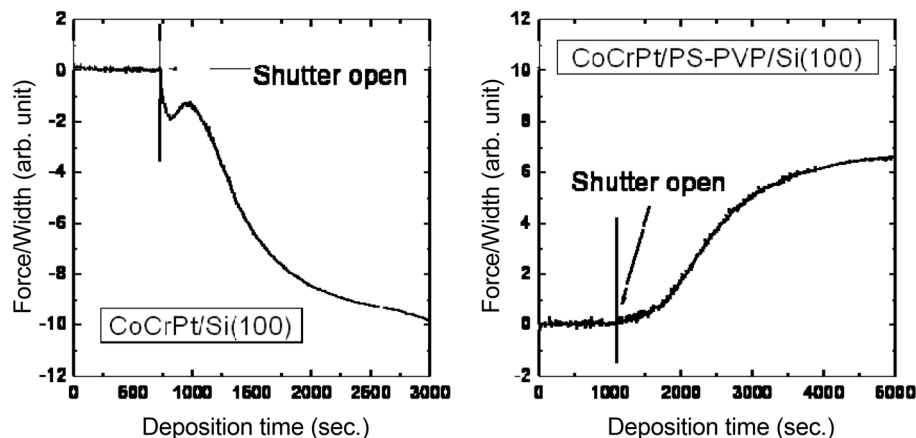


Fig. 2. Stress evolution of the CoCrPt thin film on (a) Si(100) substrate and (b) PS-PVP/Si(100) substrate.

of the CoCrPt/Si sample, very large compressive stress was observed at the initial stages of CoCrPt film deposition followed by a short period of tensile stress, as shown in Fig. 2(a). After further film deposition, it eventually relaxes to a smaller compressive stress. However, in the case of the CoCrPt/PS-PVP/Si sample, there is no significant stress development in the CoCrPt/PS-PVP/Si sample, as shown in Fig. 2(b). In particular, no large initial growth stress was observed at the initial stages of CoCrPt film deposition, which suggests that the initial growth stress in the CoCrPt/PS-PVP film is fully relaxed due to the introduction of a PS-PVP diblock copolymer buffer layer. The stress relaxation in the early stages of film growth was attributed to the soft mechanical properties of organic materials, e.g. the bulk elastic modulus of polystyrene films is 3.5 GPa [18]. Therefore, lattice misfit stress, which is one of the most important origins of interfacial stress, could be ignored due to the softness of the polymer layer. However, the magnitude of stress that developed in the thick CoCrPt region in Fig. 2(b) was half that observed in the CoCrPt/Si sample and the slopes had a different sign.

The growth structure of CoCrPt/PS-PVP films was investigated by AFM to determine the stress relaxation mechanism in CoCrPt/PS-PVP samples because the growth stress is intimately related to the growth structure of the film. Fig. 3 shows the surface morphology of the PS-PVP/Si(100), 3 nm, 6 nm and 9 nm CoCrPt/PS-PVP/Si(100) samples measured by non-contact AFM, respectively. Figure 3(a) shows that the size of the micelles is quite uniform and highly ordered with a micelle island height of 4 nm. AFM measurements of the CoCrPt/PS-PVP/Si(100) thin films deposited on a polymer surface showed that the surface morphology of CoCrPt also has regular and highly ordered spherical islands similar to the PS-PVP template, as shown in Fig. 3(b) and 3(c). The size of the islands was similar to the PS-PVP diblock copolymer micells. The Fourier transformation image obtained from the film morphology also indicated hexagonal ordering of the islands. However, the island height and root-mean-square (RMS) roughness increased drastically after 3 nm CoCrPt film deposition on a PS-PVP surface, as shown in Fig. 3(b). This suggests that the CoCrPt film follows the spherical topography of a PS-PVP template but is deposited preferentially on top of the PVP block rather than covering the mounds and valleys in a uniform manner at the initial growth stages of CoCrPt growth. However, further deposition of CoCrPt film led to a decrease in RMS roughness, as shown in Fig. 3(c) and 3(d).

Fig. 4 shows the evolution of the surface RMS roughness of CoCrPt/PS-PVP/Si and CoCrPt/Si samples as a function of the film thickness. The figure clearly shows that the roughness of the CoCrPt film on PS-PVP/Si is

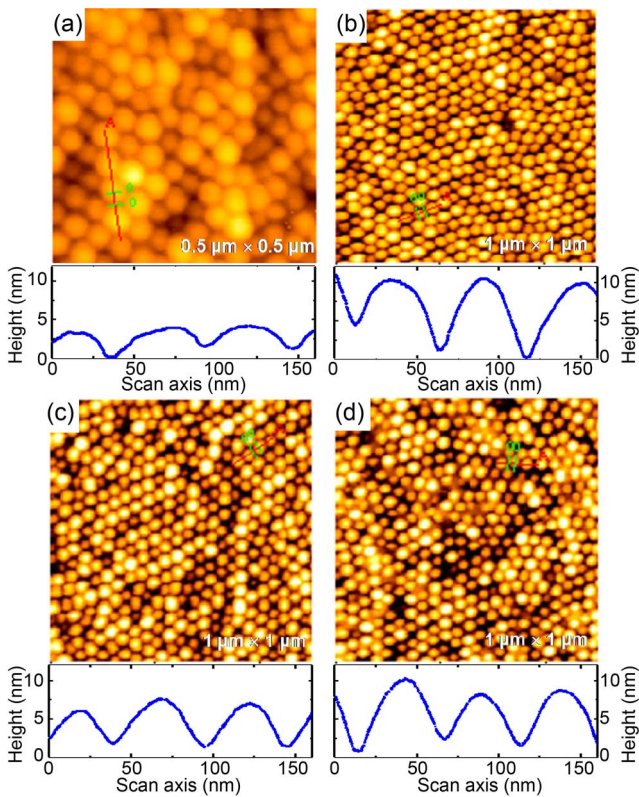


Fig. 3. (color online) AFM images and corresponding line profiles of (a) PS-PVP/Si(100) sample, (b) 3 nm CoCrPt/PS-PVP/Si(100) sample, (c) 6 nm CoCrPt/PS-PVP/Si(100) sample, and (d) 9 nm CoCrPt/PS-PVP/Si(100) sample.

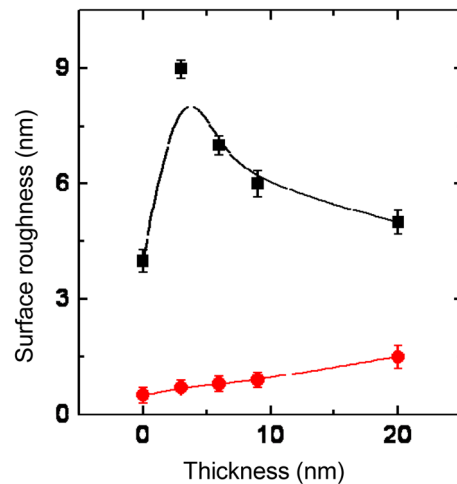


Fig. 4. Thickness dependence of the surface roughness of the CoCrPt/PS-PVP/Si(100) sample (square) and CoCrPt/Si(100) sample (circle). The solid lines are a guide to the eye only.

dependent on the film thickness. In particular, an abrupt increase in surface roughness was observed at the very initial stages of CoCrPt deposition on the PS-PVP/Si substrate, whereas the CoCrPt/Si sample showed no substantial changes during deposition. It suggests that at the initial growth stage of CoCrPt growth, the CoCrPt film deposited preferentially on top of the PVP block rather than smoothing or uniformly covering the corrugated substrate. The observed growth process of the CoCrPt on PS-PVP surface was characterized by Volmer-Weber growth mode, in which the atoms form stable clusters through a stochastic nucleation process, and the clusters grow as isolated islands, which eventually impinge and coalesce into larger islands [19, 20]. In this process, a tensile stress is generated in thin films due to the impingement and coalescence of growing islands, and the tensile stress peak is known to correlate with the formation of a continuous film structure. Therefore, it could be considered that the stress relaxation in the CoCrPt film on PS-PVP/Si substrate is strongly associated with the preferential deposition of CoCrPt films on the PVP block.

Magnetic force microscopy (MFM) measurements of 50 nm CoCrPt films were carried out to examine the effect of the polymer buffer layer on the magnetic properties. The magnetic states of the film were imaged using a Veeco Nanoscope IV with a low-magnetic moment commercial tip. The film was imaged in the demagnetized state after applying a periodic descending magnetic field.

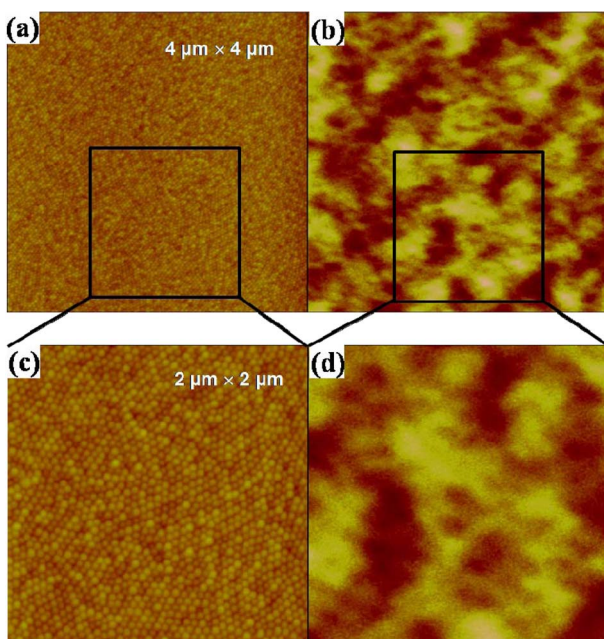


Fig. 5. Topography and corresponding phase images of a 50 nm thick CoCrPt film on PS-PVP/Si(100) substrate for (a,b) 4 $\mu\text{m} \times 4 \mu\text{m}$ and (c,d) 2 $\mu\text{m} \times 2 \mu\text{m}$ scan area.

Fig. 5 shows the topography and phase image of the 50 nm thick CoCrPt/PS-PVP films. A clear periodic corrugated surface structure of CoCrPt films due to the PS-PVP buffer layer was observed in the topography images, and typical domain microstructures could be seen in the phase images, which are consistent with the reported result, i.e. considerable differences in magnetic domain size and pattern were not observed compared to the CoCrPt thin films without a polymer buffer layer [21]. These results and a previous study on CoCrPt/PS-PVP, which showed a correlation between the perpendicular magnetic anisotropy and spherically modulated surface morphology, suggest the potential to tune the magnetic properties of CoCrPt films using a polymer buffer layer without disturbing the magnetic domain microstructure and grain size distribution, which is essential for the next generation magnetic recording media.

4. Conclusions

This study examined the growth stress of CoCrPt films on a spherically modulated polymer surface and its correlation with the growth structure. The stress that developed in the CoCrPt/Si sample was double in magnitude than that in the CoCrPt/PS-PVP/Si sample but the slope was opposite. This suggests that stress in the CoCrPt/PS-PVP film is relaxed due to the existence of a PS-PVP diblock copolymer. In addition, the introduction of a polymer layer drastically alters the stress evolution of a CoCrPt thin film. Since intrinsic stress is strongly related to the magnetic properties through magnetoelastic coupling in ultrathin ferromagnetic films, these results highlight the importance of a detailed investigation of the stress relaxation mechanism in organic/inorganic hybrid systems.

Acknowledgement

This study was supported financially by research funding from Chungnam National University in 2008.

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