ToF-SIMS Study of Carbon Diffusion in Co-Pt-TiO$_2$ Composite and Ruthenium Films

Jianhui Wang and Sam Zhang$^*$

School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798

In this paper, the diffusion behavior of hydrogenated amorphous carbon into Co-Pt-TiO$_2$ and Ruthenium films was first investigated. Impact of carbon on Co-Pt-TiO$_2$ composite film and its diffusion in Co-Pt-TiO$_2$ and ruthenium films were studied using Time-of-Flight Secondary Ion Mass Spectroscopy. Magnetic coercivity drop was observed for Co-Pt-TiO$_2$ films coated with ruthenium and carbon hybrid overcoat at varied thickness ratio. Co-Pt-TiO$_2$ film is widely used in perpendicular magnetic recording. Carbon depth profile showed that carbon readily diffuses in Co-Pt-TiO$_2$ film because of its porous structure. However, carbon diffusion in ruthenium film is limited even annealing up to 200 °C in argon. Carbon's diffusion length and coefficient in Co-Pt-TiO$_2$ are much higher than that in Ru film. The activation energy was calculated for both cases.

Keywords: Carbon, Diffusion, Ruthenium Barrier, SIMS, TEM, XRD.

1. INTRODUCTION

Hydrogenated carbon film has been used as overcoat on magnetic layer to improve anti-corrosion and mechanical performance in hard disc application. The fact that carbon readily diffuses into the magnetic layer underneath (due to its small atomic size) has caused another kind of problem.$^1$ The magnetic and tribological performance might be degraded as a result.$^{2-3}$ Thiele has pointed the coercivity drop of a cobalt based magnetic film to interaction between Co alloys and the carbon coating.$^4$ Introduction of thin barrier layer in between magnetic film and carbon overcoat may be the way out. Ruthenium (Ru) has been applied as a diffusion barrier for Cu in semiconductor device.$^5$ Recently Ru was used to impede carbon diffusion in magnetic films.$^6$ With insertion of thin Ru barrier, the magnetic film became magnetically more stable. Ru was selected due to its unique properties of high density and chemical inertness. In addition, Ru films are easily deposited by sputtering. Co-Pt-TiO$_2$ film is widely used in perpendicular magnetic recording structure. Preventing carbon diffusion in the film makes good “magnetic” sense. In the present work, the diffusion of carbon into Co-Pt-TiO$_2$ film and the effect of Ru as barrier was investigated by Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) technique.

2. EXPERIMENTAL DETAILS

Two kinds of films were deposited by magnetic sputtering on glass substrates at room temperature using a commercial sputter system MDP-250B from Inte-Vac: carbon on Co-Pt-TiO$_2$ films and carbon on pure Ru layer. A 10 nm thick Ru film was sputtered on the glass substrate as a seed layer to obtain good crystal orientation of Co-Pt-TiO$_2$ film. The sputtering of Co-Pt-TiO$_2$ films was performed at gas pressure of 50, 80, 120 mTorr. The thickness of the Co-Pt-TiO$_2$ film was about 20 nm. Samples (A) with variable ruthenium and carbon thickness were prepared on the top of the Co-Pt-TiO$_2$ film, with the total thickness of carbon and ruthenium film kept at 4 nm. The carbon film thickness was controlled at 10 nm for all samples by fixing anode voltage (60 V), and filament current (0.8 A). Sample B and C were split into 5 groups, and four of them underwent argon anneal at elevated temperatures of 50, 100, 150, 200 °C for 30 s respectively. The working
pressure of the furnace was 1 atm. The film structure of sample A, B, C was illustrated in Figure 1.

The Magnetic coercivity of Co-Pt-TiO₂ films (A) was measured by a Vertical Rotational Disc Magnetometer (VRDM). Compositional depth profile for as-deposited and post-annealed sample B and C were analyzed by ToF-SIMS depth profiling. The SIMS system used was ToF-SIMS V system manufactured by ION-TOF GmbH (Münster, Germany). Primary ion bombardment was done with 25 KeV Bi⁺ ions from a liquid metal ion gun and was rastered over an area of 100 × 100 μm². The sputter gun used Ar⁺ ions with 500 eV energy rastering over a 500 × 500 μm² area. Depth profiling was carried out in interlace mode. The apparatus was pumped down to a vacuum of 1 × 10⁻⁸ mbar prior to operation of spectrometer. Crystalline structure of the Ru film was determined using a PANalytical X’Pert X-ray diffraction (XRD) with Cu tube anode (λ = 1.5406 Å). Scanning was operated at 45 kV and 40 mA for phase identification. Symmetric θ–2θ scans were conducted ranging from 20° to 90° with a step size of 0.1°. High-Resolution Transmission Electron Microscope (HRTEM, Philips CM300) was used to study the grain structure of Co-Pt-TiO₂ composite film.

3. RESULTS AND DISCUSSION

Figure 2 shows the change in normalized magnetic coercivity (Hc) of the Co-Pt-TiO₂ films (Sample A) corresponding to Ru film thickness. Less than 3% of standard deviation is expected based on 3 samples measured for each point. The coercivity decreases as Ru film thickness is reduced. The drop of coercivity is caused by the carbon diffusion in Co-Pt-TiO₂ structure, and the impact of carbon diffusion increases as its thickness increases.² The deadlayer formation at the interface area is believed to be less evident with introduction of Ru barrier, which also minimizes the downshift of Hc. As the deposition pressure for Co-Pt-TiO₂ films goes up, the down-shifting of the Hc becomes more, owing to more diffusion of carbon into more porous Co-Pt-TiO₂ at higher argon pressure. The change in the chemical environment of the alloying elements in the structure leads to change in the magnetic properties of the Co-Pt-TiO₂ films.
To understand the results observed in Figure 2, SIMS compositional depth profiling for carbon was carried out on samples B and C. The elemental depth profile of carbon in its own bulk region and sub-interface area in CoPtTiO$_2$ and Ru films was established in Figures 3 and 4. Subplantation of carbon into CoPtTiO$_2$ was detected in the as-deposited sample as shown in Figure 3. Carbon was driven further into the bulk area of CoPtTiO$_2$ after annealing at 50 to 200 °C. The profiles clearly revealed long penetration “tails” due to diffusion. Thickness loss in carbon layer was seen for sample B annealed at 200 °C since C atoms were lost as H was released at elevated temperatures.$^7$ The interface structure in sample C was intact after annealing up to 200 °C (Fig. 4). Very limited amount of carbon atoms was detected in the subinterface area in sample C. There was no thickness loss which means with Ru interlayer the carbon layer is thermodynamically stable. This may be attributed to the higher graphitization activation energy when Ru barrier layer is present. Results obtained in Figures 3 and 4 suggested that carbon is ready to penetrate into magnetic CoPtTiO$_2$ film of porous structure during deposition, and diffuse into the sublayer under external driving force, i.e., thermal treatment. Based on the etch rate of 0.5 Å/s in CoPtTiO$_2$ for our SIMS setup, carbon diffused up to 14.4 nm deep into CoPtTiO$_2$ in as-deposited sample B. In contrast, carbon concentration remained low at the sub-interface area in sample C. Carbon diffusion in ruthenium was very little from 50 to 200 °C.

In our experiment, both CoPtTiO$_2$ and Ru films are polycrystalline. The diffusion behavior of carbon will be analyzed using the theoretical diffusion model developed by J. C. Fisher.$^8$ Fisher proposed a quantitative profile describing lattice-diffusion coupled with grain-boundary diffusion. Based on Harrisons’s classification rule$^9$ of the diffusion kinetics for grain boundary diffusion, he introduced three regimes called type A, B, and C. The kinetics observed after diffusion anneals at high temperatures, or/and with long annealing times, or/and in materials with small grain size is type A. Type C kinetics corresponds to conditions where lattice diffusion is practically ‘frozen in,’ in which diffusion takes place along grain boundaries only, without any essential leakage into adjacent grains. Our systems belong to type B kinetics regime, where the samples were annealed at lower temperatures, and with relatively short annealing time. This classification is the first and still the most widely used one for polycrystalline structure. As seen in Figure 3, diffusion profile of carbon consists of two well defined regions: one is the near-surface area dominated by lattice-diffusion and the other deep penetrating grain-boundary diffusion tail. This diffusion profile looks very similar to what was generalized by Harrisons in his kinetics classification. The lattice diffusion or bulk diffusion is believed to occur due to atomic defects in crystals, such as vacancies and interstitials. Those defects appeared more easily and frequently at the interface area because the top layers of CoPtTiO$_2$ adjacent to carbon film were exposed to plasma damage during carbon deposition. The diffusion at the second zone of a long penetrating “tail” can be explained by the granular structure of CoPtTiO$_2$ as shown in an in-plane Transmission Electron Microscope (TEM) image in Figure 5. The CoPtTiO$_2$ deposited at 80 mTorr showed a distinct granular structure with clearly segregated grain boundaries. In the image, CoPtTiO$_2$ film shows a well isolated and uniform granular structure. The averaged grain size was about 10 nm. From the TEM image, the distinct grain boundaries of CoPtTiO$_2$ film provide high-diffusivity channels for carbon diffusion, because the mobility of atoms along grain boundaries is usually much higher than in the lattice.$^8$ This explains the compositional depth profile of carbon in Figure 3 where after anneal, grain boundary tail is clearly appreciable. However, the carbon diffusion profile in Figure 4

**Fig. 4.** SIMS depth profile for carbon films coated on ruthenium.

**Fig. 5.** In-plane TEM image for CoPtTiO$_2$ film deposited at pressure of 80 mTorr.
suggested otherwise when Ru layer was present. The gradient of the line in Figure 9, which determines the type of diffusion mechanism involved in sample C, is almost flat. It is therefore believed that the diffusion in Ru was confined on surface. The insignificant amount of carbon in Ru is explained by its grain structure as measured by XRD in Figure 6. There was a minimum (100) peak intensity (at 38.25°). The intensity of (002) peak corresponding to c-axis orientation at about 42.05° was comparably small as well. No preferred orientation. All these suggested a nano-crystalline structure. Tan and others, however, observed amorphous Ru film as-deposited using ion beam sputtering. With a structure of grains in nanometer size, the Ru film in sample C is believed denser. Carbon diffusion would then become more difficult. Improvement of barrier effect through grain size reduction for copper metallization using TaN film has been demonstrated by Takeyama et al. Carbon diffusion in Ru is believed to be interstitial, not substitutional, because there is no carbide formation detected and Ru atomic size is almost twice of carbon.

Using the solution of the Fick’s Second Law of diffusion to fit the data presented in Figures 3 and 4 based on constant surface concentration, after time \( t \) at temperature \( T \), the carbon profile in the layer is:

\[
\frac{C}{C_i} = 1 - \text{erf}(x/2\sqrt{Dt})
\]

Where \( x \) is the distance from the surface, \( C \) and \( C_i \) the concentration of carbon at location \( x \) nm into the film and at the surface, respectively, and \( D \) the diffusion coefficient. The results were plotted in Figures 7 and 8 for \( C \) in Co-Pt-TiO₂ and C in Ru. To avoid clutter in the Figure 8, the fitting curves for films annealed at 50 and 150 °C are not plotted. The values of \( 2\sqrt{D} \) were obtained based on the fitting results for samples annealed at varied temperatures, and listed in Table I.

Based on data in Table I, the Arrhenius diagram was plotted in Figure 9. The linearity of the curves agrees well with the thermal dynamic description of diffusion coefficient \( D \). The Arrhenius equations for \( C \) diffusion in Co-Pt-TiO₂ and Ru were therefore obtained as:

\[
D \text{ (nm}^2/\text{s}) = 2.2596 \text{ exp}(7721 \text{ Jmol}^{-1}/kT) \quad (1)
\]
Fig. 9. Arrhenius diagram obtained from curves fitted based on diffusion from constant surface concentration model.

and

\[ D (\text{nm}^2/\text{s}) = 0.0898 \exp(2079 \text{ Jmol}^{-1}/kT) \]  

respectively, where \( k \) is Boltzmann’s constant. The preexponential factor \( D_0 \) in Eq. (1) is one to two orders of magnitude higher than that in Eq. (2), indicating the readiness of carbon diffusion in Co-Pt-TiO\(_2\) and the effectiveness of Ru as a diffusion barrier.

4. CONCLUSION

Carbon diffusion causes degradation of magnetic coercivity of Co-Pt-TiO\(_2\) composite films. Deposition of a ruthenium nanolayer effectively serves as a diffusion barrier which reduces the carbon poisoning of the Co-Pt-TiO\(_2\) magnetic film. SIMS depth profiling studies confirm that carbon readily diffuses into the granular structure of the magnetic film but the diffusion in Ru is confined at sub-surface area. This is true as tested up to 200 °C. The diffusion of carbon in Co-Pt-TiO\(_2\) is dominated by grain boundary diffusion but that in Ru is believed only superficial (surface diffusion) and interstitial. At 200 °C, the diffusion coefficient of carbon in Co-Pt-TiO\(_2\) is 0.3308 nm\(^2\)/s while that in Ru is 0.0542 nm\(^2\)/s.

References and Notes


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