Optothermal Property and Decomposition Characteristics of PtO$_x$ Ultrathin Film Sandwixed Between ZnS–SiO$_2$ for Super-Resolution Near-Field Recording

Yung-Chiun Her$^1$,* Bou-Yin Liao$^1$, Wei-Chih Hsu$^2$, and Song-Yeu Tsai$^2$

$^1$Department of Materials Engineering, National Chung Hsing University, Taichung, Taiwan 40254, Republic of China
$^2$Materials Research Laboratory, ITRI, Hsinchu, Taiwan 31041, Republic of China

We have investigated the optothermal property and decomposition characteristics of PtO$_x$ ultrathin film protected by ZnS–SiO$_2$ layers and effects of the constituent phases of PtO$_x$ on super-resolution capability and read stability of the super-RENS disk. All the ZnS–SiO$_2$/PtO$_x$/ZnS–SiO$_2$ multilayers exhibited a steep reflectivity drop at the temperature range between 265 and 350 °C, corresponding to the decomposition of PtO$_x$. The decomposition temperature of the 4-nm-thick PtO$_x$ ultrathin film protected by ZnS–SiO$_2$ layers was much lower than those obtained in thick PtO$_x$ films without protection. The activation energy for thermal decomposition was ~1.3 eV. Both the decomposition temperature and activation energy for thermal decomposition were unaffected by the constituent phases of PtO$_x$. Carrier to noise ratios (CNR) of over 40 dB for mark size of 150 nm were achieved in all super-resolution near-field structure (super-RENS) disks, while the super-resolution readout was limited to $2.5 \times 10^3$ ~ $4.5 \times 10^4$ cycles. The effect of constituent phases of PtO$_x$ on the super-resolution capability of super-RENS disk with a PtO$_x$ mask layer was minimal. However, as the constituent phases of PtO$_x$ mask layer transformed from a mixture of Pt and PtO, to pure PtO, and then to a mixture of PtO and PtO$_2$, the readout stability of super-RENS disk increased dramatically since less heat was absorbed by the PtO$_x$ mask layer composed of PtO and PtO$_2$ during the readout process, prohibiting the diffusion of materials inside the bubble to the GeSbTe phase change layer.

Keywords: Optothermal, Decomposition, PtO$_x$ Ultrathin Mask Layer, Super-RENS.

1. INTRODUCTION

The super-resolution near-field structure (super-RENS) disk, adopting a PtO$_x$ ultrathin film as mask layer, can successfully record and retrieve small marks beyond the resolution limit to achieve ultrahigh-density optical data storage.$^{1-5}$ The recording mechanism has been approved as the formation of rigid bubble pits filled with Pt nanoparticles in the PtO$_x$ mask layer through the thermal decomposition of PtO$_x$ into Pt and O$_2$, and the deformation of phase change recording layer.$^5$ However, the readout mechanism of super-RENS disk is not yet clear. Some researchers have proposed that the Pt nanoparticles are activated in the rigid bubble and scatter the light abnormally by a laser photon or thermal effect. This surface-plasmon scattering light interacts with the phase change recording layer, resulting in the huge enhancement of readout signal.$^{1,2}$

Additionally, it is reported that smaller Pt nanoparticles may reduce the threshold readout power and provide a better readout stability.$^3$ Undoubtedly, the optothermal property and decomposition characteristics of PtO$_x$ ultrathin mask layer play important roles in the recording and readout mechanisms of the super-RENS disk.

The PtO$_x$ film is normally prepared by reactive sputtering of Pt in oxygen/argon plasmas. The constituent phases of the as-deposited PtO$_x$ film are highly dependent on the experimental parameters such as oxygen flow ratio, sputtering power, and substrate temperature.$^6-8$ The polycrystalline PtO and α-PtO$_2$ phases can be obtained at higher oxygen content with substrate temperature maintained at 400 °C,$^9$ while the mixture of amorphous Pt, PtO, and PtO$_2$ phases can be prepared on the substrate with no external heating at various oxygen flow ratios.$^7$ Several groups have investigated the structural, optical, and electronic properties and thermal stability of various reactively sputtered
PtO$_2$ films with thickness ranging from 100 nm to few μm. However, none of them investigated the optothermal property and decomposition characteristics of PtO$_2$ ultrathin film sandwiched between ZnS–SiO$_2$ protective layers, which are of significance for super-resolution near-field recording. Besides, the influences of the constituent phases on decomposition characteristics of PtO$_2$ and on super-resolution capability and read stability of the super-RENS disk have not been studied yet. In this work, we investigated the optothermal property and decomposition characteristics of PtO$_2$ ultrathin films, prepared at various oxygen flow ratios, with ZnS–SiO$_2$ protective layers. The reflectivity variations of the ZnS–SiO$_2$/PtO$_2$/ZnS–SiO$_2$ multilayers with temperature were monitored in real time by a reflectivity-temperature measuring system. The decomposition temperatures, activation energies for decomposition, and structural transition of various PtO$_2$ ultrathin films sandwiched between ZnS–SiO$_2$ protective layers were determined and characterized. Super-RENS disks with PtO$_2$ ultrathin mask layers prepared at various oxygen flow ratios were also prepared and tested by an optical disk drive tester to understand the effect of constituent phases of PtO$_2$ on super-resolution capability and read stability of the super-RENS disk.

2. EXPERIMENTAL DETAILS

ZnS–SiO$_2$/PtO$_2$/ZnS–SiO$_2$ multilayers were deposited on Corning 7059 glass and silicon substrates. The 4 nm-thick PtO$_2$ films were prepared by RF reactive magnetron sputtering of a pure Pt target in Ar/O$_2$ plasma, where the sputtering power was fixed at 100 W, and the oxygen flow ratios of O$_2$/(O$_2$ + Ar) were controlled at 0.05, 0.2, and 0.5 with Ar flow kept constant at 20 sccm. The ZnS–SiO$_2$ protective layers of 20 nm in thickness were prepared by RF magnetron sputtering of a (ZnS)$_{80}$(SiO$_2$)$_{20}$ target with a sputtering power of 220 W and an Ar flow of 20 sccm. No intentional heating was applied on substrates during deposition. The constituent phases of the as-deposited PtO$_2$ films, prepared at various oxygen flow ratios, on silicon substrates were identified by grazing incident X-ray diffractometer (GIXD) and X-ray photoelectron spectroscopy (XPS). The optothermal properties of the ZnS–SiO$_2$/PtO$_2$/ZnS–SiO$_2$ multilayers on glass substrates with PtO$_2$ films prepared at various oxygen flow ratios were monitored by a reflectivity-temperature measuring system, where samples were mounted on a Linkam THMS 600 heating stage and heated to 600 °C at heating rates of 5, 10, 20, and 40 °C/min in an argon protective atmosphere. The reflectivity variations with temperature for the multilayered samples were recorded in real time. To correlate the optothermal property with decomposition behavior of PtO$_2$ ultrathin film, the structural phase transitions and optical properties of the ZnS–SiO$_2$/PtO$_2$/ZnS–SiO$_2$ multilayers on silicon substrates before and after thermal annealing were characterized by GIXD and measured by a UV-visible spectrophotometer, respectively. Secondary ion mass spectroscopy (SIMS) was also utilized to analyze the elemental distributions in the ZnS–SiO$_2$/PtO$_2$/ZnS–SiO$_2$ multilayers. The super-RENS disks with a layer structure of ZnS–SiO$_2$ (170 nm)/PtO$_2$ (4 nm)/ZnS–SiO$_2$ (20 nm)/GeSbTe (20 nm)/ZnS–SiO$_2$ (40 nm) on polycarbonate substrates were prepared, and tested by an optical disk drive tester (DDU-1000, Pulstec Industrial Co.), with a wavelength of 635 nm and a numerical aperture of 0.6. Accordingly, the theoretical resolution limit is 265 nm. After a series of dynamic tests were performed, the multilayered ZnS–SiO$_2$/PtO$_2$/ZnS–SiO$_2$ prepared at various oxygen flow ratios were irradiated by a 405 nm blue laser pulse, with a power of 8 mW for the duration of 250 ns, and then examined by field-emission scanning electron microscope (FE-SEM) and transmission electron microscopy (TEM).

3. RESULTS AND DISCUSSION

Figure 1(a) shows the GIXD diffraction patterns of the as-deposited ZnS–SiO$_2$/PtO$_2$/ZnS–SiO$_2$ multilayers, with PtO$_2$ prepared at various oxygen flow ratios. No diffraction peak was found in all three samples except a very
weak board band, indicating the constituent phases of the as-deposited PtO, ultrathin films prepared at various oxygen flow ratios were amorphous. The same amorphous phases were also observed in the as-deposited PtO, films with thicknesses of 4 and 20 nm by Kolobov et al. using X-ray absorption spectroscopy. In order to understand the constituent phases in the amorphous PtO, ultrathin films prepared at various oxygen flow ratios, the binding energies of Pt 4f7/2 and 4f5/2 were measured by XPS, as shown in Figure 1(b). Here a pure Pt metallic film was also prepared and measured. The binding energies of Pt 4f7/2 and 4f5/2 for Pt metallic film were measured to be 71.2 and 74.6 eV, respectively, which agree very well with reported data. For PtO, films prepared at an oxygen flow ratio of 0.05, the Pt 4f7/2 and 4f5/2 peaks were found to have shifted to 72.3 and 75.6 eV. As the oxygen flow ratios were further increased to 0.2 and 0.5, the Pt 4f7/2 and 4f5/2 peaks would further shift to 73.8 and 77.1 eV, and 74.0 and 77.3 eV, respectively. According to the Handbook of X-ray Photoelectron Spectroscopy, the binding energies of Pt 4f7/2 and 4f5/2 for PtO and PtO2 are reported to be 73.8 and 77.1 eV, and 74.6 and 77.9 eV, respectively. At an oxygen flow ratio of 0.05, the Pt 4f7/2 and 4f5/2 peaks of PtO, film were located in between those of pure Pt and pure PtO, suggesting the PtO, film was composed of a mixture of amorphous Pt and PtO phases. As the oxygen flow ratio was increased to 0.2, the locations of Pt 4f7/2 and 4f5/2 peaks of PtO2 film were exactly the same as those of pure PtO, indicating the PtO, film had formed an amorphous PtO phase. As the oxygen flow ratio was further increased to 0.5, the Pt 4f7/2 and 4f5/2 peaks of PtO2 film were positioned in between those of pure PtO and pure PtO2, indicating that the PtO, film was composed of a mixture of amorphous PtO and PtO2 phases. It is evident that as the oxygen flow ratio was increased, the constituent phases of PtO, film progressively transformed from a mixture of Pt and PtO phases, to a pure PtO2 phase, and then to a mixture of PtO and PtO2 phases, because more oxygen radicals were supplied to react with Pt atoms during the sputtering process. These results are similar to those reported by Abe et al., though the corresponding oxygen flow ratios for the transitions between Pt, PtO, and PtO2 may be slightly different due to different experimental parameters.

To analyze the opothermal property of PtO2 ultrathin film protected by ZnS–SiO2 dielectric layers, the reflectivity variations with temperature for the multilayered samples with PtO2 films prepared at various oxygen flow ratios were monitored by a red laser with a wavelength of 635 nm at a heating rate of 40 °C/min, as shown in Figure 2. All the curves exhibit a steep reflectivity drop at the temperature range between 265 and 350 °C, which was confirmed to be caused by the occurrence of thermal decomposition of PtO2 into Pt and O2. The thermal decomposition temperature of PtO2 ultrathin film protected by ZnS–SiO2 dielectric layers, defined as the temperature at the onset of reflectivity drop, was found to be approximately 265 °C, and was nearly unaffected by the oxygen flow ratio. It is worthy of note that the decomposition temperature we obtained was significantly lower than those obtained in PtO2 films of 100 nm to a few μm in thickness without any protection, where the decomposition temperatures of around 550 ~ 600 °C were reported. However, similar decomposition temperatures between 230 and 500 °C have been observed by Saenger et al. in the first stage of a two stage decomposition reaction occurring in a 100 nm-thick PtO2 film. Recently, Kolobov et al. also reported that the decomposition process of a 4-nm-thick PtO2 layer sandwiched between ZnS–SiO2 layers starts at temperatures around 520 K (247 °C) and is completed at temperatures around 650 K (377 °C) through the in situ X-ray absorption near-edge structure (XANES) studies. Saenger et al. suggested PtO2 film would start decomposing to Pt at a temperature well below 400 °C from the top surface of the film, and the formation of thin surface layer of Pt would act as a diffusion barrier for further oxygen release, so that the second stage of decomposition would not take place, until the thermal driving force for PtO2 decomposition could overcome the oxygen trapping effect of the thickening surface barrier layer of Pt. As the thickness of PtO2 film is only 4 nm in the present experiment, the decomposition of the PtO2 ultrathin film is believed to be mainly dominated by the first stage of decomposition so that a much lower decomposition temperature was obtained. However, Kikukawa et al. showed that 15 nm PtOx film without ZnS–SiO2 layers has the same decomposition temperature (~850 K) as those reported for the 100 nm film. It is believed that in addition to the oxygen trapping effect, the film stress induced by the sample configuration may be considered as another key factor affecting the decomposition temperature of PtO2.

Fig. 2. Reflectivity variations with temperature for ZnS–SiO2/PtO2/ZnS–SiO2 multilayers prepared at various oxygen flow ratios.

with film thickness in the early stages of film growth, and a stress level of ~1800 MPa can be developed after the film grows above a certain thickness.\(^{15}\) As the PtO\(_x\) film was also prepared by reactive sputtering, the 4-nm-thick PtO\(_x\) ultrathin film is expected to possess a lower compressive stress than those PtO\(_x\) films with thicknesses above 100 nm. Therefore, a smaller amount of thermal energy will be consumed in the 4-nm-thick PtO\(_x\) film to release of film stress before the occurrence of decomposition, resulting in a lower decomposition temperature. Similar stress effect on Al-induced crystallization of a-Si was reported by Hsu et al.\(^{16}\) Although the beginning temperature of thermal decomposition was independent of the oxygen flow ratio, the complete temperature of thermal decomposition of PtO\(_x\) ultrathin film protected by ZnS–SiO\(_2\) layers was found to increase with the oxygen flow ratio. It may be caused by the progressive transformation of constituent phases of PtO\(_x\) film from a mixture of Pt and PtO to a mixture of PtO and PtO\(_2\) phases when the oxygen flow ratio was increased. Because the bonding energy between Pt and O in PtO\(_x\) is higher than that in PtO, a higher temperature would be required to complete the decomposition process. After the first stage of thermal decomposition of PtO\(_x\) ultrathin film was completed, the reflectivity of the multilayered samples reached a saturated value in the temperature range between 350 and 500 °C, and then increased gradually with temperature above 520 °C. The increase in reflectivity is may be attributed to the aggregation of the decomposed Pt metallic particles to form larger Pt metallic clusters through surface diffusion. From the viewpoint of thermodynamics, small Pt nanoparticles prefer to form larger Pt metallic clusters to reduce the total surface free energy once the activation energy for atomic diffusion can be overcome. As the total surface area to scatter the incident light will decrease as well, leading to the increase in reflectivity. During the cooling process, the reflectivity of the multilayered samples remained unchanged, representing that the thermal decomposition of PtO\(_x\) ultrathin film protected by ZnS–SiO\(_2\) layers was an irreversible process. As the irreversible decomposition of PtO\(_x\) ultrathin mask layer will take place during the recording process, the super-RENS disk with a PtO\(_x\) mask layer may be considered as a write-once and read-many disk.

Figure 3 shows the GIXD diffraction patterns of ZnS–SiO\(_2\)/PtO\(_x\)/ZnS–SiO\(_2\) multilayers prepared at various oxygen flow ratios, after being heated to 500 °C and cooled down to room temperature. As expected, only Pt was detected in all ZnS–SiO\(_2\)/PtO\(_x\)/ZnS–SiO\(_2\) multilayers due to the decomposition of PtO\(_x\) into Pt and O\(_2\). To further verify the irreversibility of thermal decomposition of PtO\(_x\) ultrathin film protected by ZnS–SiO\(_2\) layers, the room temperature depth profiles of Pt, O, Zn, S, and Si in the ZnS–SiO\(_2\)/PtO\(_x\)/ZnS–SiO\(_2\) multilayers, before and after annealing at 420 °C for 3 min were analyzed by SIMS, as shown in Figure 4. In the as-deposited state, PtO\(_x\) film was clearly sandwiched between the two ZnS–SiO\(_2\) protective layers. After annealing at 420 °C for 3 min, the decomposed Pt metallic element was still confined at the same position, however, the released O\(_2\) was found to diffuse toward the protective layers and became trapped at the
interfaces between PtO$_x$ and ZnS–SiO$_2$. Meanwhile, S element from the ZnS–SiO$_2$ protective layers was also found to diffuse into the PtO$_x$ film. These evidences strongly support that the thermal decomposition of PtO$_x$ ultrathin film protected by ZnS–SiO$_2$ layers is an irreversible process. Moreover, since S element can easily react with O$_2$ to form sulfur oxide, it may promote the decomposition of PtO$_x$ ultrathin film and result in a lower decomposition temperature.

As the heating rate was increased, the corresponding decomposition temperature of PtO$_x$ ultrathin film protected by ZnS–SiO$_2$ dielectric layers would increase. The relationships between heating rate and decomposition temperature can be expressed by the Kissinger’s equation:\textsuperscript{17}

$$\ln\left(\frac{\alpha}{T_i^2}\right) = C - \left(\frac{E_a}{RT_i}\right)$$

Here, $\alpha$ is the heating rate, $T_i$ is the absolute decomposition temperature, $C$ is a constant, $E_a$ is the activation energy for thermal decomposition, $R$ is the gas constant. By plotting $\ln(\alpha/T_i^2)$ versus $(1/T_i)$, linear relationships would be established and the activation energies for thermal decomposition of PtO$_x$ ultrathin films, prepared at various oxygen flow ratios can be determined from the slopes of the straight lines. Figure 5 shows the Kissinger’s plots for ZnS–SiO$_2$/PtO$_x$/ZnS–SiO$_2$ multilayers prepared at various oxygen flow ratios. The activation energies for thermal decomposition of PtO$_x$ ultrathin films protected by ZnS–SiO$_2$ dielectric layers were determined to be 1.28 ± 0.07, 1.26 ± 0.02, and 1.22 ± 0.02 eV/atom, respectively, as the oxygen flow ratios of 0.05, 0.2, and 0.5 were applied. Those values are fairly close to the effective activation energy of 25 kcal/mol (∼1.1 eV/atom) for the first stage of decomposition of 100 nm-thick a-PtO$_x$ reported by Saenger et al., and are significantly lower than that of 71 kcal/mol (∼3.1 eV/atom) for the second stage of decomposition at ∼600 °C,\textsuperscript{5} confirming that the thermal decomposition of the 4-nm PtO$_x$ ultrathin film resembles the first-stage of decomposition of the 100-nm-thick PtO$_x$ film, and can occur at a temperature well below 600 °C.

Figure 6(a) shows the dependence of carrier to noise ratio (CNR) on mark size in the super-RENS disks with PtO$_x$ mask layers, prepared at various oxygen flow ratios. Here, the optimum writing and reading powers were set to be 15 and 4 mW, respectively, by a series of tests. It was seen that CNR of 42, 45, and 43 dB were obtained at the mark size of 150 nm in the super-RENS disks with PtO$_x$ mask layers, prepared at the oxygen flow ratios of 0.05, 0.2, and 0.5, respectively, while CNR of about 27 dB was obtained at the mark size of 100 nm in all disks. Obviously, the super-resolution readout can be successfully achieved by the super-RENS disk with a PtO$_x$ mask layer, and the super-resolution readout signal was only slightly affected by the constituent phases of PtO$_x$. Figure 6(b) shows the dependence of CNR on reading cycle for 150-nm mark trains in the super-RENS disks with PtO$_x$ mask layers prepared at various oxygen flow ratios. It was found that the super-resolution readout of the super-RENS disks would fail after reading cycles of $2.5 \times 10^3$, $2.5 \times 10^4$, and $4.5 \times 10^4$ when the PtO$_x$ mask layers were prepared at oxygen flow ratios of 0.05, 0.2, and 0.5, respectively. Evidently, the readout stability of the
super-RENS disk dramatically increased with the oxygen flow ratio. To understand the effects of constituent phases of PtOₓ on super-resolution capability and readout stability of the super-RENS disk, the ZnS–SiO₂/PtOₓ/ZnS–SiO₂ multilayers were irradiated by a 405 nm blue laser pulse with a power of 8 mW for the duration of 250 ns, through an objective lens with a numerical aperture of 0.65 to simulate the recording process, and then examined by TEM, as shown in Figures 7(a) to (c). The blue laser power was chosen to be 8 mW, so that the power received per unit area on the sample is equal to that irradiated by a 635 nm red laser of 15 mW, which is the optimum recording power obtained in the dynamic tests. It is seen that numerous Pt nanoparticles with diameters ranging from few nm to tens of nm were precipitated in the laser-irradiated regions in all multilayered samples through the decomposition of PtOₓ, and the multilayer with PtOₓ prepared at a higher oxygen flow ratio formed a smaller decomposed area. As we examined the morphology of the laser-irradiated region in ZnS–SiO₂/PtOₓ/ZnS–SiO₂ multilayer by FE-SEM, a rigid bubble pit with a length of ~200 nm, created by the O₂ gas pressure, was clearly observed, as shown in Figure 8. The precipitation of nano-sized Pt metallic particles and formation of rigid bubble pits, have been observed by Kikukawa et al. from the cross-sectional TEM images of the sample disk after the recording process. During the readout process, the surface-plasmon scattering light around the Pt nanoparticles inside the bubble pits interact with the deformed recording layer, explaining the huge enhancement of the readout signals at the mark lengths smaller than the resolution limit. It should be noted that the bubble pits themselves have nothing to do with super-resolution readout and the Pt particle are the origins of the super-resolution readout of the disk. As all the three super-RENS disks with PtOₓ mask layers consisted of different constituent phases have similar precipitation of Pt nanoparticles in the bubble pits during recording, a similar super-resolution capability will be expected. Regarding the readout stability, Kim et al. have reported that the readout stability of the super-RENS disk with a PtOₓ mask layer is strongly related to the damage of the GeSbTe phase change layer, caused by the diffusion of materials inside the bubble. Since the decomposition temperature of PtOₓ ultrathin film is nearly unaffected by the oxygen flow ratio, the readout stability of the super-RENS disk may depend on the absorptance of PtOₓ mask layer. Figure 9 shows the wavelength dependence of the absorptance of ZnS–SiO₂/PtOₓ/ZnS–SiO₂ multilayers prepared at various oxygen flow ratios in the as-deposited and annealed states. At the wavelength of 635 nm, the absorptance of the annealed ZnS–SiO₂/PtOₓ/ZnS–SiO₂ multilayer decreased from 33% to 29 and 27%, as the oxygen flow ratio increased from 0.05 to 0.2 and 0.5, respectively. Since the annealed ZnS–SiO₂/PtOₓ/ZnS–SiO₂ multilayer prepared at a lower oxygen flow ratio exhibited a higher absorptance, more heat would be absorbed by the PtOₓ mask layer during the readout process, and more intensive diffusion of materials.
inside the bubble to the GeSbTe phase change layer will be expected. As a result, the super-RENS disk prepared at a lower oxygen flow ratio will be more easily deteriorated by thermal activated diffusion, leading to worse readout stability.

4. CONCLUSIONS

The constituent phases of the reactively sputtered PtOₓ film gradually transformed from a mixture of Pt and PtOₓ to pure PtO, and then to a mixture of PtO and PtOₓ, as the oxygen flow ratio was increased. Thermal decomposition of the 4-nm-thick PtOₓ ultrathin film protected by ZnS–SiOₓ layers occurred at a temperature (~265 °C) much lower than those (~550 °C–600 °C) obtained in PtOₓ films of 100 nm to a few µm in thickness without any protection. The activation energies for decomposition of PtOₓ ultrathin film protected by ZnS–SiOₓ layers were found to range from 1.22 to 1.28 eV/atom. The super-resolution readout can be successfully achieved by the super-RENS disk with a PtOₓ mask layer, where the precipitation of Pt nanoparticles and formation of rigid bubble pits were observed after recording. As the constituent phases of PtOₓ mask layer transformed from a mixture of Pt and PtOₓ to pure PtO, and then to a mixture of PtO and PtOₓ, the super-resolution capability of the super-RENS disk was nearly unaffected, while the readout stability increased dramatically.

Acknowledgments: This work was sponsored by the National Science Council of the Republic of China under Grant No. NSC92-2216-E-005-010. The authors would like to thank Edward Young for reviewing the manuscript.

References and Notes


Received: 16 January 2006. Accepted: 1 April 2006.