Terabit-per-square-inch Phase-change Recording on Ge-Sb-Te Media with Protective Overcoatings

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Key Words : Phase-change, Ge-Sb-Te, probe-based storage, AFM, protective coating

ABSTRACT

We reported here nano-scale electrical phase-change recording in amorphous $Ge_2Sb_2Te_5$ media using an atomic force microscope (AFM) having conducting probes. In recording process, a pulse voltage is applied to the conductive probe that touches the media surface to change locally the electrical resistivity of a film. However, in contact operation, tip/media wear and contamination could major obstacles, which degraded SNR, reproducibility, and lifetime. In order to overcome tip/media wear and contamination in contact mode operation, we adopted the W incorporated diamond-like carbon (W-DLC) films as a protective layer. Optimized mutilayer media were prepared by a hybrid deposition system of PECVD and RF magnetron sputtering. When suitable electrical pulses were applied to media through the conducting probe, it was observed that data bits as small as 25 nm in diameter have been written and read with good reproducibility, which corresponds to a data density of 1 $Tbit/inch^2$. We concluded that stable electrical phase-change recording was possible mainly due to W-DLC layer, which played a role not only capping layer but also resistive layer.

1. Introduction

Owing to the high areal density and small form factor, scanning probe microscope (SPM) based storage technologies have drawn much attention in both scientific and industrial aspects. Since the report of the "millipede" data storage concept, which is based on the parallel operation of a large number of probes [1], atomic force microscopy (AFM)-based data storages have been spotlighted for applications, because the data rate could be increased substantially. On the other hand, phase changing materials such as Ge-Sb-Te and Ag-In-Sb-Te alloys are commonly used as rewritable storage media, since they show a strong dependence of optical and electrical properties upon structure. In practically thin films of Ge-Sb-Te alloys are currently used in optical memories such as rewritable digital versatile disk-random access memories (DVD-RAM).[2]

In recent times, there have been some reports on reversible recordings in amorphous Ge-Sb-Te films using an atomic force microscope (AFM) having conducting cantilevers.[3-4] The principle behind phase change recording is the reversible transformation of local region in the active layer between the stable crystalline (high conductivity) and the metastable amorphous phases (low conductivity). In recording process, a pulse voltage is applied to the conductive probe that touches the media surface to change locally the electrical resistivity, that is, an amorphous area increases the local temperature above phase-change temperature which enables the crystallization of amorphous bit. Recorded data could be read by monitoring the local electrical conductance differences. However, in contact operation, tip/media wear and contamination could be major obstacles, which degraded the SNR, reproducibility, and lifetime. Only a few studies have reported in the view point of topographic changing.

In this paper, we have focused on the stable nano-scale electrical phase-change recording in amorphous $Ge_2Sb_2Te_5$ film using a conductive AFM. In order to overcome this tip/media wear and contamination, we adopted the W incorporated diamond-like carbon (W-DLC) films as a protective layer. As a result, , we could

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observed that data bits as small as 25 nm have been written and read without severe topographic changing due to protective layer acting as both capping and suitable resistance layer.

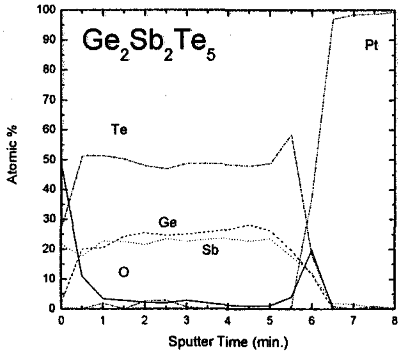


Fig. 1 Chemical composition profile of as-deposited Ge-Sb-Te film.

2. Experiment Procedure

GST films with the thickness of 20 and 100 nm were deposited at room temperature on both a Si(100) and Pt(200nm)/SiO$_2$/Si substrate by the hybrid deposition system of r.f.-PECVD and RF magnetron sputtering. This system allowed the continuous W-DLC top layer deposition as protective layer. Base pressure of vacuum system was less 10^{-7} torr. GST films were deposited by sputtering Ge$_2$Sb$_2$Te$_5$ composite target in Ar gas with RF power set to 20 mtorr and 150 W. W-DLC films were deposited by sputtering a high purity W target using Ar and CH$_4$ as the sputtering gas and applying 13.56 MHz of r.f. power to the substrate. The fraction of CH$_4$ in the sputtering gas was varied to change the W concentration in deposited film. X-ray diffraction measurements showed that as-deposited GST films were amorphous. Composition of GST films was measured by Auger spectroscopy. In order to verify phase-change behavior of the deposited GST films with temperature, the specimens were also annealed in a rapid-thermal-process (RTP) at various temperatures for 15 min in an Ar environment. The electrical resistivity of films was measured using a four-point probe system. Topographic and conductance images of films were analyzed using a scanning probe microscope (SPM, PSIA ltd. XE-100), that was operated in an ambient atmosphere and in the contact mode with conductive coated Si tip. The spring constant of the cantilevers was around 0.1 N/m. Writing process was conducted by applying a negative pulse voltage between -5 and -7 V to the probe, which were produced by a pulse generator with GPIB computer control system. The written data were read using a positive DC voltage ranging from +0.5 to +1 V to substrate at scanning speed of 1 um/sec.

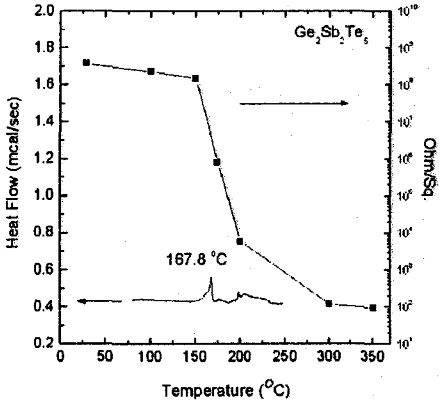
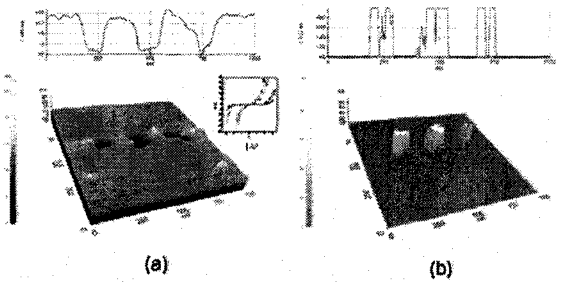


Fig. 2 DSC curves and electrical resistivity as a function of temperature.

3. Results and discussion

Figure 1 shows the composition depth profile of the as-deposited GST films measured by Auger spectroscopy. All elements of Ge, Sb, and Te are uniformly distributed through the film maintaining the ratio of 2:2:5. However, it must be noted that there were also the surface oxide layer which caused by the natural oxidation. Kooi *et al* reported that the strong effect of oxidation of the GST film on the crystallization behavior.[5] It will be discussed later conjunction with the result of W-DLC/GST film.

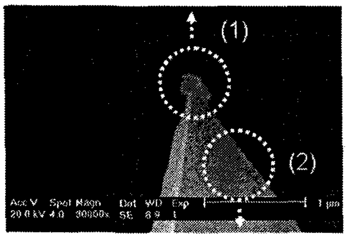
Figure 2 shows the dependence of electrical resistivity on temperature of a Ge$_2$Sb$_2$Te$_5$ film. The resistivity was suddenly decreased above 150 °C which meant the phase-change was occurred. To confirm the phase-change temperature, differential scanning calorimetry (DSC) analysis was also employed. As shown in Fig. 2, the crystallization temperature corresponds to peak from DSC. At the heating rate of 10 C/min, the measured crystallization temperature was around 160 °C, which corresponding to phase transition in the amorphous phase to a face-centered cubic phase of crystalline structure.[6] It was well agreed with result of four-point probe measurement.



(a) (b)

Fig. 3 (a) Topographic and (b) conductance images after 3 point writing process in as-deposited Ge$_2$Sb$_2$Te$_5$ film. I-V curve was also added.

	Al	Si	P	Ni	Au
Atomic %	1.94	6.66	0.61	9.66	82.24



	Al	Si	P	Ni	Au
Atomic %	0.51	0.64	0.63	7.72	90.70

Fig. 4 SEM image of used Au coated tip after writing process. EDX analysis was also added.

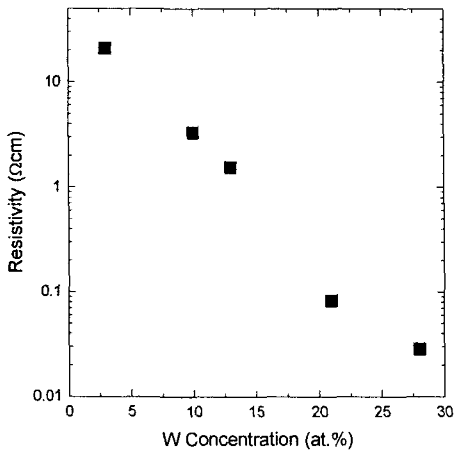


Fig. 5 Electrical resistivity of W-DLC films with W concentration.

Previously, Gotoh *et al* pointed out the difference of low and high voltage marks.[4] They observed that low-voltage mark (under -4 V), which formed by carrier injection without any structural changes, had the short retention time. In this work, we also observed unstable writing results at the low-voltage. In realizing storage devices, the retention time and reproducibility is considered to be the important factor. Thus, the writing process was carried out by applying pulse voltages of -5 V for 500 ns to the probe, while the probe was scanned on the sample surface. Fig. 3(a) and (b) show the typical topographic and conductance image read at +1 V, respectively, after applying of the pulse voltages at three points. Higher conductance points formed where the pulse voltages were applied. It was arise from that electrical resistance difference due to the Joule heating-induced phase-change. As can be seen in Fig. 3(a), current-voltage curves of the treated and untreated region are clearly different. However, although considering the volume reduction due to the changing of density [7], there were severe topographic changes at written marks in the topographic images shown in Fig 3(a). Maximum depth of concave mark was about 14 nm. In order to investigate the reason of that, SEM/EDX analysis was conducted. Fig. 4 shows the ESEM image of used Au coated tip after three point writing operation. The damage of tip apex with higher Si concentration indicated that there was an excessive Joule heating above the melting temperature of Au coating. In the case of Pt coated tip, the same tendency was also observed. We concluded that the severe topographic change was mainly due to damaged tip and surface oxide layer of $Ge_2Sb_2Te_5$ film shown in Fig. 1.

In order to overcome this tip/media wear and the surface oxidation, we adopted the diamond-like carbon (DLC) films as a protective layer. Although DLC films were well known as protective overcoatings due to their high wear resistance, low friction coefficient, and smooth surface [7], but they have high electrical resistivity. Thus, we adopted W incorporation into the DLC during the deposition to control the resistivity. As shown in Fig. 5, the increasing of W concentration decreased the resistivity of DLC film. Adequate value of resistivity should not only be high enough to avoid electrical shorting, but also be low enough to detect the difference between crystalline and amorphous state. Through repeated experiments and calculations, we found that the optimum resistivity value of the protective layer was in the range of 1 - 10 Ω cm. These values are comparable to the reported value [9], in which they introduced both of top capping layer and bottom resistive layer. In this work, we determined the protective layer to have 7 Ω cm and around 1 nm thick in view point of electrical, chemical, and tribological requirements.

Fig. 6 show the composition of optimized media with the DLC top layer having 4 at.% W. It could be also seen that there were few oxide layer in the film surface.

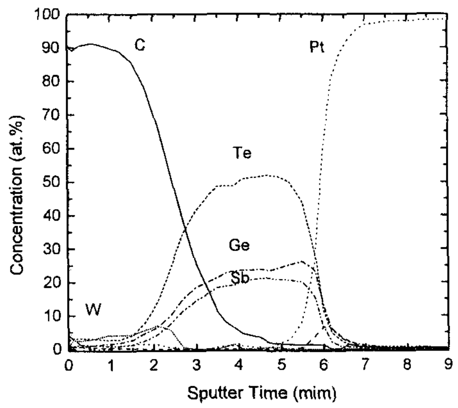


Fig. 6 Chemical composition profile of W-DLC/ $Ge_2Sb_2Te_5$ film.

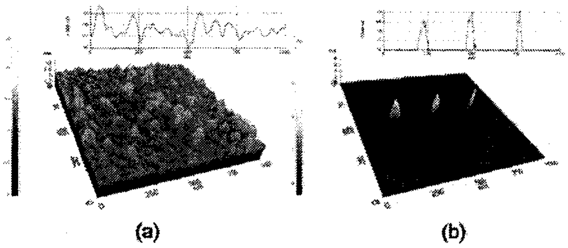


Fig. 7 (a) Topographic and (b) conductance images after 3 point writing process in W-DLC/ $Ge_2Sb_2Te_5$ film.

In the writing process, applying pulse voltage set to -6 V for 500 ns slightly higher than those used in without protective layer, because the writing probability was decreased at the same condition as shown in Fig 2. We could observe that the size of the written mark depended on the pulse width, applied voltage, and loading force.

Fig. 7(a) and (b) show the typical topographic and conductance image, respectively after the writing process at three points. Even though higher conductance points also successfully formed where the pulse voltages were applied, there was clear difference in topographic image compared with Fig. 2(a). The severe topographic changing was not observed under the same recording condition. As shown in Fig. 7(b), the smallest possible recording region was 25 nm in diameter; on the other hand the corresponding topographic changing was under a few nm. Gidon *et al* suggested that a resistive underlayer must be introduced in the electrical phase-change recording. [9] They explained that the resistive underlayer could limit the current density to sustainable values to avoid the injection of excessive power into a too small volume, eventually leading to local destruction of the media. In this work, we also observed the writing process was not well achieved in the case of W-DLC having too high resistivity. In the case of too low resistivity value, on the other hand, sudden damage of tip was often found accompanying with topographic changes. Thus, we could conclude that stable electrical phase-change recording was possible mainly due to W-DLC layer, which played a role in not only a capping layer but also a suitable resistive layer.

The introduction of protective layer would be a key to reach the ultrahigh densities in probe-based electrical phase-change recording media.

4. Conclusions

We demonstrated the stable nano-scale electrical phase-change recording in amorphous $Ge_2Sb_2Te_5$ film using a conductive AFM. In order to overcome the tip/media wear and oxidation, we adopted the W-DLC films as a protective layer. As a result, when electrical pulses were applied to media through the conducting probe, it was observed that data bits as small as 25 nm in diameter had been written and read without severe topographic change, which corresponds to a data density of 1 Tbit/inch^2. We concluded that stable electrical phase-change recording was possible mainly due to W-DLC layer, which played a role not only capping layer but also suitable resistive layer.

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