

# Macroscopic Study on Etching Characteristics of Phase-change Recording Films

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## ABSTRACT

We developed a phase-change etching (PCE) technique in which only crystalline regions in a phase-change (PC) recording film were etched by an alkaline solution. This technique enables phase-change mark observation or fabrication of small patterns using phase-change recording. We found that etching rates depend not only on PC films but also on annealing conditions and aging of samples whose difference could not be observed by measuring their reflectivity. We discussed the mechanism of this technique based on experimental results of etching rates and surface energy of a PC film.

## I. INTRODUCTION

Phase-change (PC) optical recording is now used in rewritable optical discs such as CD-RW, DVD-RAM, DVD  $\pm$  RW, and Blu-ray Disc (BD). At the moment, studies are in progress on applications of PC techniques not only for optical discs but also for semiconductor memories called “phase-change RAM” or “Ovonic Unified Memory”<sup>1)</sup>.

We reported on a PCE technique in which we can etch only the crystalline regions and in which amorphous regions remain on the sample surface<sup>2)</sup>. We also showed that PC recording was suitable for small-size fabrication such as 1/10 of the fabricating spot size. We should therefore anticipate nanotechnology using PC recording techniques. We have clarified, however, very little about this etching phenomenon. We have to clarify the basic properties of this phenomenon to apply this technique to fabrication.

Our aim was to firstly introduce the results previously reported, and furthermore, to clarify some fundamental aspects of etching characteristics of the PCE technique by some macroscopic experiments and to discuss its mechanism using the experimental results.

## II. OUTLINE OF PHASE-CHANGE ETCHING

This section briefly introduces an outline of PCE already reported elsewhere<sup>2)</sup>. The concept of PCE is shown in Fig. 1. We found that a sample with a PC film with crystalline and amorphous regions can be formed into pit patterns by being dipped in an alkaline solution. When we applied this technique, we could clearly observe PC marks recorded in a DVD-RW disc. Furthermore, we could fabricate dot patterns of approximately 40 nm using an optical system in the Blu-ray Disc format (Fig. 2). As we have shown by a simulation, PC recording is suitable for small-size

fabrication due to recrystallization during recording, which is an advantage unique to PC recording. Using this property and the PCE technique, we can expect a new technical field “phase-change nanotechnology”.

### III. EXPERIMENTS AND RESULTS OF BASIC PROPERTIES

First, we investigated the etching rate, which is essential data not only for applying the PCE technique to fabrication, but also for elucidating the mechanism of this phenomenon. We also describes the effect of aging of a PC film on PCE, and observe the results of wettability of a PC film surface during PCE, which is considered important for clarifying the mechanism of the PCE phenomenon.

#### A. Measurement of Etching Rate

For measuring the etching rate, samples with the following structure were used: glass substrate, transition-metal oxide (10 nm), and PC film (30 nm). All films were deposited by sputtering. A transition-metal oxide film was used to adhere the glass substrate to the film. In etching, the sample was dipped in the etching solution, which was alkaline with various pH values. In the experiment, we measured the relationship between the etching time and the PC film thickness by measuring the reflectivity of the sample in the etching solution with a spectrophotometer (Fig.3). The relationship between the reflectivity of the sample and the PC film thickness was measured before the experiments. We measured the PC films in both as-deposited and crystalline states. The as-deposited state was almost equal to the amorphous state. We created the crystalline state by annealing the samples in the oven in air.

The PC film investigated was  $\text{Ge}_5\text{Sb}_{70}\text{Te}_{25}$ . To crystallize the sample, we annealed it at  $200^\circ\text{C}$  for one minute.

Measurement results for the relationship between the etching time and the PC film thickness (as an example) are shown in Fig. 4. This shows that the as-deposited state was much more resistant to etching than the crystalline state. The qualitatively same behavior was observed for other kinds of PC films like  $\text{Ge}_2\text{Sb}_2\text{Te}_5$ ,  $\text{AgInSbTe}$ , and Ag-doped  $\text{Ge}_2\text{Sb}_2\text{Te}_5$ , although the etching rates depended on the kinds of PC films.

Figure 5 shows the relationship between the pH values of the etching solution and the etching rate of the crystalline and as-deposited states of  $\text{Ge}_5\text{Sb}_{70}\text{Te}_{25}$ . The etching rate was substituted by the thickness etched in one hour from the start of etching. This figure shows that the etching rate, as expected, was higher for higher pH values, which indicates that the mechanism of this etching phenomenon was an interaction between the PC film and the ions of the etching solution.

#### B. Aging of As-deposited Films and Etching Rate

In general, the as-deposited state or amorphous state is not stable because its energy is considered

to be higher than the crystalline state. From this, we could expect that the etching rate of the as-deposited state depended on the time passed since the film was sputtered, i.e. the age of the film.

In this experiment, we used  $\text{Ge}_5\text{Sb}_{70}\text{Te}_{25}$  and we sputtered the samples in the same batch. Etching rates were measured for samples whose ages after deposition were a few minutes (0 hr), three hours, and one month. The results are shown in Fig. 6. This figure clearly reveals that durability against etching in the as-deposited state depended on age, which was considered to have resulted from partial crystallization of the films. Since reflectivity of these samples was exactly the same, the crystallized regions must be so microscopic that they did not affect the macroscopic optical properties.

### **C. Observation of Wettability of a PC Film Surface**

We were able to observe that a drop of the etching solution spontaneously moved away from the place where it was originally. The drop stayed still for two minutes after it had been placed. It then moved away from its original place and stopped again. This kind of phenomenon is known as a “running drop”, originating from variation of the interfacial energy by a chemical reaction between the drop and the sample surface<sup>3)</sup>. From this experiment, we speculated that the interfacial energy between the sample surface and the drop became higher than the “fresh” surface. Accordingly, the drop moved to this “fresh” surface to lower the energy.

Next, we focused on the difference of the interfacial energies for the PC film in the crystalline or as-deposited state. A drop of the etching solution was placed on a PC film that had been partially crystallized by a PC disc initializer (produced by Hitachi Computer Peripherals Co.). After one minute, the drop was repelled on the crystalline surface and moved to the as-deposited surface. This indicated that the interfacial energy between the crystalline PC film surface and the drop after being etched a little was higher than the interfacial energy between the as-deposited PC film surface and the drop.

## **IV. DISCUSSIONS**

As stated in reference 2, the mechanism of this etching phenomenon must be closely related to the fact that in general amorphous metals have much stronger durability against corrosion than crystalline ones. This fact can be explained by a model in which an amorphous surface obtains a homogeneous oxidized surface that works as a chemically passive surface, while a poly-crystalline surface has grain boundaries or segregations that can be triggers for corrosion. Although the mechanism of PCE is still unknown, this model is consistent with the experimental results described above.

From the results described in III. C, we can speculate on three facts: 1) the PC film has at least two regions, *i.e.*, a surface layer and an inner bulk region whose surface energies are different, 2)

the surface energy of the crystalline surface ( $s_{cry,surf}$ ) is smaller than that of the crystalline bulk ( $s_{cry,bulk}$ ), and 3) the surface energy of the as-deposited surface ( $s_{as,surf}$ ) is almost equal to that of crystalline surface. That is,  $s_{as,surf} \approx s_{cry,surf} < s_{cry,bulk}$ . If we assume that the surface is an oxide layer generated by natural oxidation, this might be reasonable for the following reasons: 1) the electrical polarizability of the oxygen-doped GeSbTe was expected to be higher than that of pure GeSbTe, and 2) generally an electrically polarizable solid surface is wettable (Zisman's rule)<sup>4</sup>.

We can see from the results shown in Fig. 4 that the etching rate was slower in the beginning of etching. This might be due to the surface layer having corrosion resistance, *i.e.*, a slow etching rate. If this surface layer was sufficiently corrosion-resistive and sufficiently homogeneous on the as-deposited or amorphous state, this surface layer could be a strong barrier against etching.

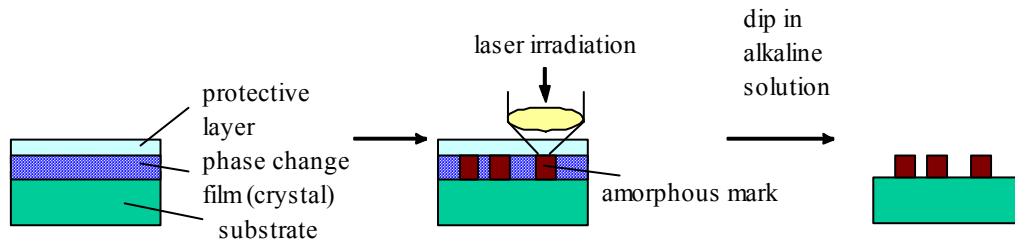
As stated above, the experimental results shown in this paper are consistent with the model for corrosion resistance of amorphous metals. The above discussions, however, are simply assumptions and speculations. To elucidate the details of PCE, we require further studies, *e.g.*, microscopic analysis.

## V. CONCLUSIONS

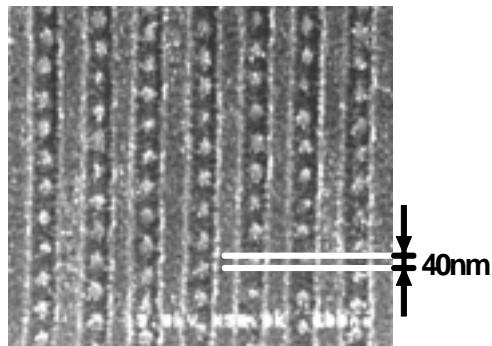
We macroscopically investigated etching characteristics of phase-change (PC) recording films and related phenomena. All the PC films investigated were found to show the same etching selectivity, *i.e.*, the etching rate of the crystalline state was much higher than that in the amorphous state. We also found that the etching rate was higher in solutions with higher pH values. From observation results on the interfacial energy of the PC film surface and the etching solution, the PC film surface has a surface layer that has a different surface energy from that of the inner bulk region. This indicated the possibility that this surface layer was a cause of anti-etching characteristics of the as-deposited or amorphous state.

## References

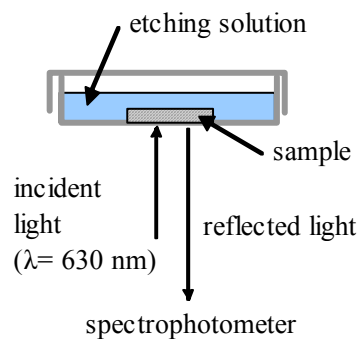
- 1) T. Ohta, W. Czubytyj, T. Lowrey and D. Strand, *Proceedings of the 15<sup>th</sup> Symposium on Phase Change Optical Information Storage 2003*, 42 (2003)
- 2) T. Shintani, Y. Anzai, H. Minemura, H. Miyamoto and J. Ushiyama, *Appl. Phys. Lett.*, Vol. 85, No. 4, 26 July 2004.
- 3) P. G. de Gennes, F. Brochard-Wyart, D. Quéré, “*Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves*” (Springer-Verlag New York) translated by A. Reisinger, p.280 (2004)
- 4) P. G. de Gennes, F. Brochard-Wyart, D. Quéré, *ibid*, p.18.



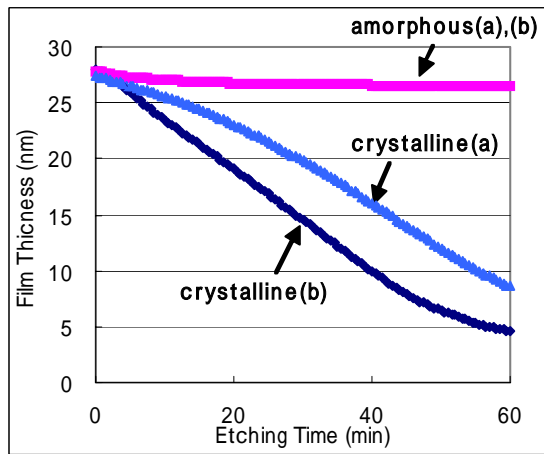
**Fig.1 Concept of Phase-Change Etching**



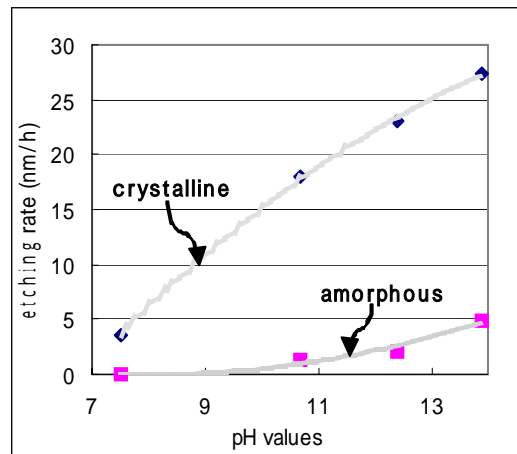
**Fig. 2 40-nm dot pattern fabricated using PCE technique. Blue-laser far-field system was used for recording.**



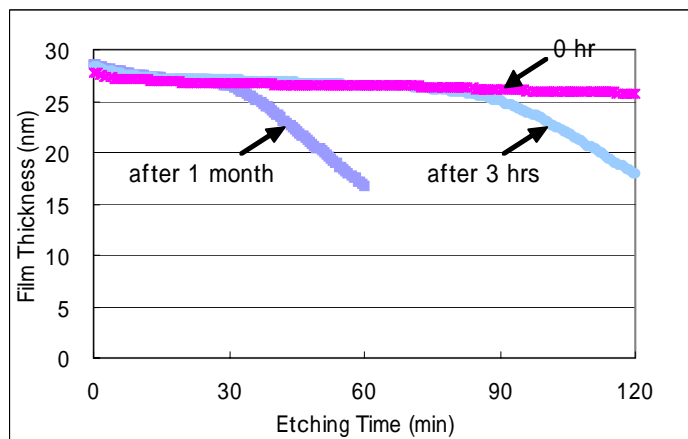
**Fig. 3 Configuration for measurement of etching rate**



**Fig.4 Relationship between etching time and film thickness <eGST,(a)pH10.5,(b)pH12.2>**



**Fig.5 Relationship between pH values and etching rate <eGST>**



**Fig. 6 Etching characteristics of three amorphous samples with different ages after deposition.**