Along with GeSbTe
- Finding the alloy and applying it to optical disks -

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ABSTRACT

It is not too much to say that our finding of the GeSbTe phase-change material in 1987 was achieved after changing the viewpoint of our material quest from the "amorphous materials" to the "crystalline materials." Some fundamental issues almost instantly disappeared and it led to the first product in 1990. It is surprising that the GeSbTe continuously answered our expectations since then. This will be owing to the unique crystalline structure and the crystallization process.

Key words: GeSbTe, phase-change, optical disk, crystalline phase-change material, serendipity

1. Introduction

It is a great honor and pleasure to give the keynote at E*PCOS meeting in this memorial year celebrating 90th birthday of Dr. S.R. Ovshinsky. As is well known, he is the farther of the phase-change (PC) science and technology; his proposal of PC memory and switching devices around 1970 strongly encouraged many researchers and technologists to study the attractive phenomenon [1]. Today, his founding has resulted in the success of the optical disk industry since 1990s and the recent energetic development of the electrical memory devices. Panasonic has studied PC technology since early 1970s and contributed to establish the novel and huge optical disk market such as DVDs and Blu-ray Disks. It would not be meaningless to summarize our activity in the R/D of PC optical memory in this occasion. I would like to start with the brief history of our material quest and next describe how we reached to GeSbTe and applied it to the various optical disk products.

2. Early stage of the PC material quest

From 1970s to the first half of 1980s, R/D activities for requiring the ideal PC alloys were mainly concentrated on the so-called "amorphous materials." The materials consisted of Te as a main component and small amounts of cross-linking additives such as Si and Ge (four-fold) and As and Sb (three-fold). It can be said that the chief issues in this field were "how to obtain a good amorphous forming material" and "how to rapidly transfer it to the crystallization phase". It is a bit symbolic that the historic paper of Feinleib et al. in 1971 involved the words, "crystallization of amorphous semiconductors" [2]. Despite of various exploratory experiments, it was increasingly dominant that the "amorphous PC alloys" would not satisfy the some essential requirements for optical memory devices.

At that time, since 10 years to the beginning of 1980s, Panasonic was developing a sub-oxide PC materials, TeOx, that was found by Ohta et al.[3]. It possessed nice properties such as high thermal stability of amorphous state and the large optical changes that were inherently suitable for an optical memory. We tackled to improve the crystallization speed of the material for applying it first to the write-once type optical memory [4] and second to the rewritable type one. After all, the first purpose was achieved and TeOx film has been applied for various write-once type products still today. The second purpose was not successful; however the experience we obtained there was very precious for our development of the rewritable PC materials hereafter. The exploratory experiments gave us much information: how the additives affected on the PC properties of Te-based alloy. For example, we become to see that Au or Pd addition into TeOx dramatically increased the crystallization speed [5, 6] while similar noble metal, Ag or Cu, did not at all. Similarly, Ge addition into the TeOx very much increased the thermal stability of the amorphous state, and Sn substitution for some part of the Ge increased the crystallization speed at the sacrifice of optical contrast [7]. With the experimental information, we planed the next stage of material quest.

3. From the amorphous PC material to the crystalline PC material

I. Close relation between crystallization process and process

In 1986, we found a remarkable result indicating that the crystallization time closely related with the crystallization process. The crystallization time of $(Te_{80}Ge_{15}Sn_5)_{1-x}Au_x$ film dramatically decreased from 20 μs to 300 ns with the increased Au content from zero to 25 %. At this time, a very essential change occurred secretly in the crystalline phase; i.e., the crystalline phase for x=0 had a multi-phase however that for x=0.25 changed to a single-phase having a simple cubic structure [8, 9] (Fig. 1). This result just caused us to become aware of the importance of the crystalline structure or the crystallization process of PC materials. Around the same time, Chen et al. reported the distinguishing difference of the crystallization properties between the eutectic composition, $Ge_{15}Te_{85}$, and stoichiometric compound, GeTe [10]; thus, we were convinced that the appearance of the single phase in the crystallization process would be essentially important for the nanosecond rapid crystallization.

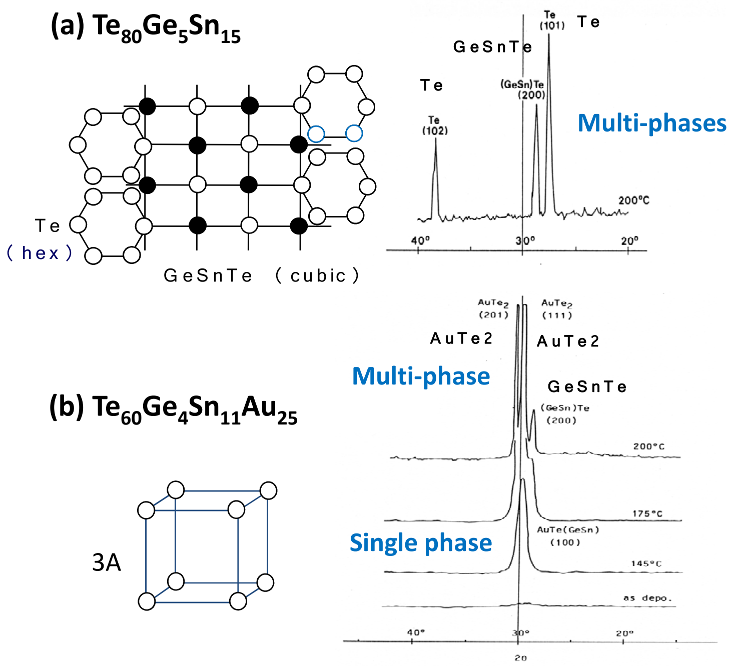

Fig.1 Large change of the crystallization process of Te80Ge5Sn15 by addition of Au [8,9]

II. Amorphous formation of Ar

According to the progress of computer technologies, the scientific calculation such as the molecular dynamics simulation was just becoming general around 1986. One pioneering result was the amorphous formation of Ar shown by Yonezawa et al.[11]. It was proven that even a noble gas element, Ar, could be transformed to the amorphous phase when it was cooled down at the very large cooling rate of 10^{12} K/sec. In fact, this report very much encouraged us, since we had obtained a thermal simulation result that the very large cooling rate around 10^{10} K/sec could be achieved by combining the laser quenching technology and the thin film stack of an optical disk [12]. Thus, we obtained another way for leading to the ideal PC alloys. It was "how to obtain essentially crystalline materials" and "how to effectively transfer it to the amorphous phase".

4. Finding of GeTe-Sb_2Te_3 pseudo binary PC materials

We narrowed down the scope for our material quest into the Te-Ge-α ternary systems and refined their compositional dependence including stoichiometric compounds. At first, some quaternary systems Te-Ge-α including a small amount of Se were examined aiming the effect of Se of assisting amorphous formation ability and increasing the thermal stability of the amorphous phase; however, it became soon apparent that Se was not indispensable. Among the various candidates, finally two alloys of Te-Ge-Sb and Te-Ge-Bi were found to show remarkable phase-change characteristics. Their crystallization temperature were sufficiently high, sometimes more than 200C, and the crystallization time by laser heating were very short, less than 100 ns. It was noted here that these alloys displayed a unique and curious phenomena; i.e., their fine PC characteristics widely ranged with centering the GeTe-Sb_2Te_3 or

$GeTe$-Bi_2Te_3 tie line. By XRD, ED and DSC analyses (Fig. 2), it was identify that a single phase with cubic structure appeared in the wide compositional range for each case) [13]. The appearance of the metastable cubic phase over wide range was indeed a "serendipity" leading us to the success of the PC optical memories. Since then, our long journey along with GeSbTe has started [14].

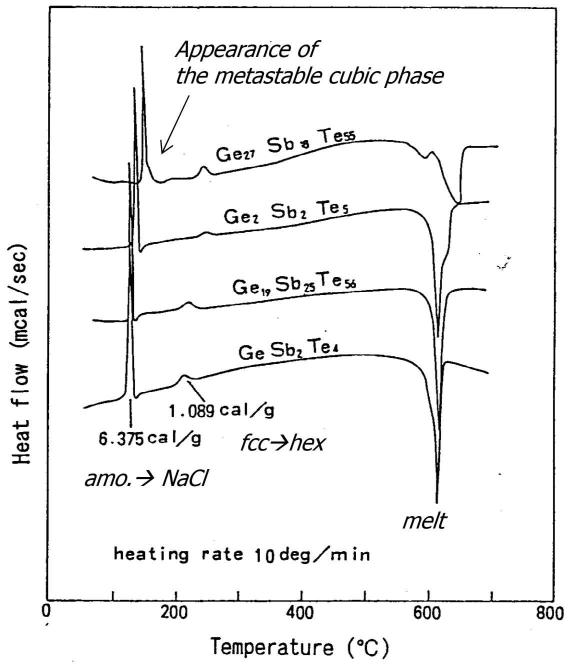

Fig. 2 Observation of the appearance of metastable phase in the GeTe-Sb2Te3 pseudobinary films (DSC) [13]

5. Optical disk applications

Since 1990, Panasonic has commercialized the large number of rewritable PC optical disks such as DVD-RAMs and Blu-ray Disks utilizing the GeSbTe and GeBiTe (Fig. 2). During the long period, these two PC alloys have well lived up to our expectations. This is because their phase-change characteristics could be rather easily modified. The controlling of the crystallization time and thermal stability could be achieved just by changing the ratio among the three components and also by substituting the component for the other elements. The essential merits of GeSbTe and GeBiTe were kept as they are despite of the rather large modification such as N dope and Sn substitution for Ge etc.[15,16]. I think it is owing to their unique crystalline structure and crystallization process [17, 18].

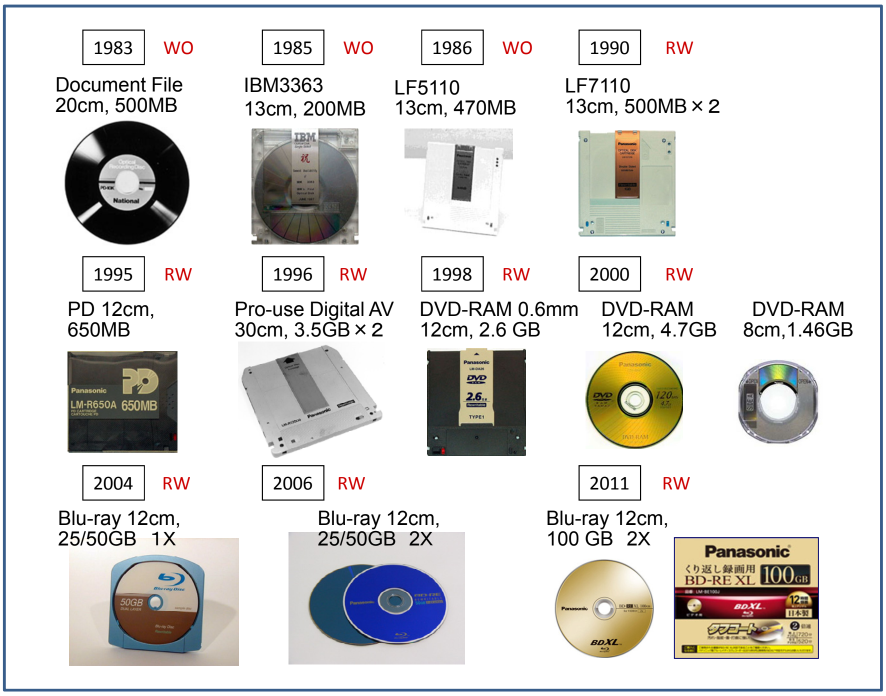

Fig. 3 PC optical disk products of Panasonic since 1983: labels of WO and RW denote write-once and rewritable, respectively.

In the optical disk developments, not only the optimization of PC film but the structure designing of disk structure was very essential for overcoming the next stage issues: many recording-erasing cycles and very long term data retention time. In this viewpoint, novel dielectric films were developed and the layer stack was optically and thermally refined [19, 20]. With the many technologies, the latest product of the triple layer Blu-ray Disc with 100 GB capacity was launched in the market last year, where the very thin PC films were piled up and the recording-reading was achieved freely on each layer using just one laser beam [21].

6. Conclusion

In 1997, we obtained a chance to invite Dr. Ovshinky to Panasonic. At the occasion, we could hear his new study toward the multi-level electric memory using the GeSbTe. It was a large pleasure for me that our work was closely resonant with the new idea of the farther of PC technologies. During the long period for developing the PC optical disks, many analytical studies have been actively carried out on the unique structure and the rapid phase-change mechanism of the GeSbTe. The technologies and the scientific knowledge that have been obtained there will contribute to the next pronounced progress of the electrical devices. I hope furthermore it will lead to the new generation optical memory again.

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Biographies

Noboru Yamada graduated from Kyoto University in 1974 and joined Central Research laboratories of Panasonic. Since then, he has studied phase-change optical memory materials and optical disks by utilizing the materials. His typical achievements were the founding of GeSbTe alloys and the world-first products of 4.7GB DVD-RAM and 50GB Blu-ray Disk as the research leader. He obtained his Ph.D. from Kyoto University in 2001. He is now a technical advisory staff at the Advanced Technology Research Laboratories of Panasonic.