# PHASE-CHANGE OPTICAL MEMORY PROMOTES THE DVD OPTICAL DISK

### T. Ohta

Optical Disk Systems Development Center, Matsushita Electrical Industrial Co., Ltd. 1006 Kadoma, Kadoma City, 571-8501 Osaka, Japan

The progress in phase-change optical disk memory, based on amorphous chalcogenide materials is presented. High density recording of around 100 Gb/in<sup>2</sup> was reached. The basic effect of the ultra short laser pulse of femto second response on phase-change film for the future Tb/s data rate recording is discussed.

(Received June 26, 2001; accepted September 11, 2001)

Keywords: Phase-change memory, Optical disk, Amorphous chalcogenide

## 1. Introduction

Great advances have been made in memory devices such as magnetic tapes, floppy disks, hard disks (HDDs) and semiconductor memory such as memory cards. The density growth rate of HDDs is around 60% /year but the upper limit of density due to paramagnetic stability is thought to be around 50 Gbits/in<sup>2</sup>. Hard disks have high speed data transfer rates but are generally not removable.

Optical disk memory has its own unique feature of read-only media performance, which is also compatible with the rewritable function and is different from HDD technology. Recordable optical disk market such as CD-R is growing recently and the shipment becomes 3 billions disks/year. Rewritable optical disk technology was first commercialized in the form of the magneto-optical (MO) disk. With the increasing use of multimedia, phase-change rewritable (PCR) optical disks are becoming more popular due to their CD and DVD (digital versatile disk) compatibility.

In 1968, S. R. Ovshinsky discovered a new memory phenomenon in chalcogenide film materials. This order-disorder phase-change memory effect came to be called the "Ovonic memory" [1]. In developing this storage medium, the main issues have been the stability of the film materials, the stability of the reversible cycle characteristics and the recording sensitivity. The author and his colleagues were the first to achieve a breakthrough in these areas, which led to the commercialization of phase-change optical disk products. The first version phase-change optical disk product was shipped in 1990 from Matsushita/Panasonic. The PD (phase-change dual) and CD-RW (rewritable) followed, and now rewritable DVD with 4.7 GB capacity and 3.4 Gbit/in<sup>2</sup> density is being produced.

Blue laser technology, large numerical aperture lens, volumetric recording and multilevel recording technologies are candidates for the future of high-density phase-change nanometer scale mark recording technology.

This paper describes the breakthroughs achieved, the progress on phase-change optical disk memory of the candidate of the high-density recording with a density of around 100 Gbits/in<sup>2</sup> and more, and discusses the basic effect of the ultra short laser pulse of femto second response on phase-change film for the future Tbit/s data rate recording.

## 2. Principle of overwrite phase-change memory

### 2.1. Phase-change optical memory phenomena

Prior technologies developed for optical disk memory in 1972 utilized thin film materials of either the thermal deformation type or ablation pit mark forming type. These methods, however, require rather high laser power, while is difficult to provide rewritable performance. In the first stage I

proposed sub-oxide thin film phase-change memory by  $\text{TeO}_x$  and developed W/O (write-once) optical disk products for video image file optical disk system in 1982 [2]. Then I have started development of rewritable phase-change optical disk which is compatible with the W/O optical disk having the multifunction optical disk system.

There have been many kinds of rewritable thin film materials in sub-oxide system such as  $GeO_x$ ,  $SbO_x$ ,  $MoO_x$  and so on, and the chalcogenide system. As deposited films are in amorphous state and after heating, they show the darkening effect. Fig. 1 shows the optical transmission change through the heating process of the rewritable chalcogenide film.



Fig. 1. Transmission (d = 633 nm) change of GeTe-Sb<sub>2</sub>Te<sub>3</sub>-Sb (g = 2.0, b = 0.5) film when heated in air at a heating rate of 100 °C/min.

#### 2.2. Model of the phase-change memory

Fig. 2 shows the model of phase-change memory. The enthalpy of the amorphous state and the crystalline states are different. It is higher in the amorphous phase than in the crystalline phase. When the strucure changes from the amorphous state to the crystalline state, the optical absorption edge of the material shifts to shorter wavelength region. Then, the optical constant of complex refractive index N = n + ik (n is refractive index and k is extinction coefficient) changes. And the reflectivity of the film changes, which shows the optical memory effect. So, the information can be detected by the reflectivity change just like the CD disk playback method. When a high power level laser spot irradiates the crystalline film at "a", the temperature of the portion goes over the melting temperature  $T_m$ , the state changes "b" to "c" and "d".

After the laser spot moves away, the temperature goes down rapidly through super cooling state between "c" and "e" to room temperature "f". When the cooling rate is above the critical cooling rate (3.4 K/ns), the portion of the film at "f" becomes the amorphous phase. When a low power level laser spot irradiates on the amorphous mark portion "f", the temperature goes up to above "e" at the glass temperature  $T_g$ , then the amorphous portion transforms to the crystalline phase and the mark is erased.



Fig. 2. Model of the phase-change memory.

### 2.3. Phase-change overwriting method

Fig. 3 illustrates the operating principle of phase-change overwriting [3, 4]: a) shows a laser power modulation waveform, b) shows written marks on a track before and after overwriting, c) shows a readout signal after overwriting.



Fig. 3. Direct overwriting method by optical mean only on phase-change optical disk.

The critical cooling rate has been estimated to be 3.4 K/ns from our experiments [5]. The critical cooling rate depends on the atomic elements and their compositions [6].

The portion on the track irradiated by the recording high laser power is melted and after the laser spot moves away from that portion, it is quenched immediately. This quenching process changes the portion to be an amorphous mark portion. If irradiated by the erase laser power, the temperature goes up over the crystallizing temperature and the former recording mark portion changes to the erased crystalline phase. Fig. 4 shows TEM observations of the overwritten marks on the phase-change optical disk. The amorphous mark portion (a) shows hallo diffraction pattern and the erased mark portion (b) shows fcc crystalline structure diffraction pattern. The track pitch Tp is 1.2  $\mu$ m in the figure. This method achieves one-pass overwriting by using only the laser power modulation scheme. The read out signal is obtained by detecting the reflectivity change between the amorphous mark portion and the crystalline area, which is the same method as the CR-ROM signal detection method.



Fig. 4. TEM observation of overwritten marks. (a) amorphous mark, (b) erased mark.

# 3. Phase-change materials for optical memory

### 3.1. Bonding features of chalcogenide phase-change materials

Chalcogenide compounds have characteristics of easy transition from crystalline state to amorphous state. The compounds are composed of Te, Se and/or S elements which are the 6<sup>th</sup> group

elements in the Periodic Table. Fig. 5 shows the variations of the bonding structures of chalcogenide compounds.



Fig. 5. Bonding structures of chalcogenide materials
(a) Hexagonal chain structure of Te and Se [7]
(b) Ring structure of As<sub>2</sub>Se<sub>3</sub> [8]
(c) Amorphous structure of As<sub>25</sub>Te<sub>75</sub> [9].

Fig. 5(a) shows the chain structure of Te and Se crystalline [7]. Fig. 5(b) shows the network structure of the ring bonding structure produced by adding As component [8]. Fig. 5(c) shows the amorphous network structure of  $As_{25}Te_{75}$  compound [9].

The reason why these compunds are easy to transform to the amorphous state is related to the fact that the elements such as Te and Se have chain-like bonding structure.

There are two types of bonding forces, the one is covalent bonding and the other is the rather weak van der Waals force which appears in chain-chain bindings. These two different types of bonding forces are considered to relate to easy amorphizing characteristics of chalcogenide materials.

The crystalline structures of the chalcogenide materials belong to hexagonal or monoclinic systems. The former forms a spiral chain bonding structure and the later often forms a ring bonding structure with eight corners. Additive elements such as Sb and As generate bridges between chains or transform them to network structures.

#### 3.2. Phase-change disk materials for optical disk memory

The rewritable optical memory phenomena has been observed in  $Te_{81}Ge_{15}Sb_2S_2$  composition material [10]. This material was modified from  $Te_{85}Ge_{15}$  eutectic composition by adding Sb and S elements. Fig. 6 shows the phase diagram of the Ge-Te system [11]. At the eutectic composition, the melting temperature goes down to 375 °C.

The melting temperature shows a minimum at the eutectic composition, and it is expected that the viscosity increases also. Then, it is easy to freeze the bonding structure in the disordered liquid phase through the cooling process. Though many materials having easy amorphizing characteristics, were proposed in this early stage, these were typical samples for only the observation of phase-change write-erase phenomena.

In the next stage, applicable materials were found which have rather high speed crystallization characteristics. There are three kinds of phase-change material systems such as In-Sb-Te [12], Ge-Te-Sb [13] and Ag-In-Sb-Te [14]. Fig. 7(a), (b), (c) shows the phase-diagrams of In-Sb-Te, GeTe-Sb<sub>2</sub>Te<sub>3</sub>-(Sb) and the thin film structure of Ag-In-Sb-Te [14].

They exhibit different crystallization processes.

<In-Sb-Te>

This material shows that the crystalline growth phenomena overcome the nucleation rate phenomena. When erase laser power irradiates the mark written track, whose power just melts the In-Sn-Te film, then recrystallizes the portion from the mark edge and the erase ratio increases. The In-Sb-Te film and the special overwrite laser power level leads to very high erase ratio. In this case, the difference of the write peak power and the erase power is small, both are situated at the melt power level and the power tolerance of writing and erasing becomes small.



Fig. 6. Phase diagram of Ge-Te system.

### <GeTe-Sb<sub>2</sub>Te<sub>3</sub>-Sb>

The phase-change processes of the Ge-Sb-Te amorphous material were examined by DSC (differential scanning calorimetry) measurement. Fig. 8 shows that there are two exothermal peaks and one endothermal peak.



Fig. 7. Phase-change active layer materials for optical disks.
(a) In-Sb-Te ternary alloy
(b) GeTe-Sb<sub>2</sub>Te<sub>3</sub>-(Sb) system
(c) Phase-change model for Ag-In-Sb-Te system.

The first exothermal peak corresponds to the crystallization phase-change and the second to the fcc to hexagonal crystalline structure change, and the third endothermal peak corresponds to melt phase transition [15]. The latent heat for the transformation crystalline to liquid (16.3 kcal/kg) and amorphous to liquid (8.5 kcal/kg) were obtained experimentaly.

The nucleation rate overcome the crystalline growth. The erased (crystallized) state of the GeTe-Sb<sub>2</sub>Te<sub>3</sub>-Sb film shows a lot crystalline grains. It shows two steps of the erase process: in the first step, a high number of the crystalline nuclei appears and in the second step the crystalline grain growth occurs and the amorphous mark can be erased. The erase process is in the solid state and the power tolerance becomes rather wide and applicable but the erase ratio is lower than In-Sb-Te films.

Phase-change materials for overwriting by one laser spot need to have high-speed crystallizing characteristics. High-speed crystallizing materials such as the In-Se system were discovered [3].

We found a GeTe-Sb<sub>2</sub>Te<sub>3</sub>- $\langle$ Sb> system, one of the group of Ge-Te-Sb compositions, and the parameters g = GeTe / Sb<sub>2</sub>Te<sub>3</sub>, b =  $\langle$ Sb> / Sb<sub>2</sub>Te<sub>3</sub>, which control the crystallizing speed around 100 ns to 30 ns and the crystalline grain size smaller, and the residual Sb element in the system is  $\langle$ Sb> [16], [17], [18].

Recently at ODS2001, there were proposed for high density and high data rate recording, phase-change optical disks, with small amorphous mark forming, several crystallizing growth dominant compositions at the eutectic composition system such as  $Sb_{69}Te_{31}$  were propesed [CAPut!'], [20]. Last years, the density of the phase-change optical disk was increased, when the mark became small (<200 nm), and in the growth dominant case the mark can crystallize rapidly. The eutectic composition of  $Sb_{69}Te_{31}$  is the point ( $\lambda$ ) on the line of  $Sb_2Te_3$  to Sb of Fig. 9, the composition point is that of 0.18 ( $Sb_2Te_3$ ) and 0.82 Sb. The reason why this eutectic composition shows the rapid crystallization characteristics is now under discussions.



Fig. 8. DSC (differential scanning calorimeter) analysis of Ge-Sb-Te film at a heating rate of 10 °C/min.

<Ag-In-Sb-Te>

The Ag-In-Sb-Te system has two kinds of typical composition area, one is (AgSbTe<sub>2</sub>+In-Sb) system and the other is (AgInTe<sub>2</sub>+Sb) system. The phase-change model of this system is that the former composition shows that a part of the compound such as AgSbTe<sub>2</sub> crystallizes in amorphous In-Sb. This composition has large erase ratio characteristics. The origin of the erase ratio is discussed as it has low thermal conductivity components in thin film structure which is composed of the mixture of AgSbTe<sub>2</sub> phase-change component and amorphous In-Sb. The overwrite cycle performance of Ag-In-Sb-Te system is reported as around 10,000 or more and the limitation of this overwrite cycle is discussed now.



Fig. 9 The crystallizing temperature of the system. This material system shows nucleation dominant crystallizing characteristics.

### 4. Key technologies of the phase - change disk media

In the early phases of its development, the most important subject of phase-change optical disk was cycle degradation. Fig. 10 shows a cross-sectional TEM (transmission electron microscopy) image of the basic 4-layer structure of a phase-change optical disk. The layers comprise a bottom dielectric layer (155 nm), an active layer (24 nm), an upper dielectric layer (45 nm) and a reflection layer (100 nm).

Fig. 11 shows a high resolution TEM image of ZnS and the new ZnS-SiO<sub>2</sub> mixture dielectric protection films. The grain size of ZnS-SiO<sub>3</sub> film is very small, at around 2 nm [21]. The new ZnS-SiO<sub>3</sub> dielectric layer is thermally stable and does not show grain growth even after annealing at 700° C, 5 min. Grain growth in the ZnS layer was one reason the phase-change optical disks degraded after many rewrites. The newly developed materials of GeTe-Sb<sub>2</sub>Te<sub>3</sub>-Sb active layer and ZnS-SiO<sub>2</sub> protective layer have resolved one of the cycle issue of variations of signal amplitude and noise level. The other cycle degradation model is that of the sub-nanometer level space deformation of the disk layers, which works as the motive force of the sub-nanometer displacement of the active layer components. The deformation occurs by thermal expansion of the layers along the thermal diffusion process. The deformation is generally asymmetrical along the laser scanning direction, the forward edge and the backward edge.



Fig. 10. Cross-sectional TEM observation of the basic 4-layer phase-change optical disk.

The space deformation becomes the motive force of the sub-nanometer displacement of the liquid phase active layer components. The thermal expansion coefficient of SiO<sub>2</sub> is  $5.5 \times 10^{-7}$ , and of ZnS-SiO<sub>2</sub> is  $6.1 \times 10^{-6}$ . When forming an additional SiO<sub>2</sub> layer, the thermal deformation of the space between the bottom upper dielectric layer is reduced.

Subsequently, in 1989, dynamic overwrite cycle characteristics over more than  $2 \times 10^6$  cycles were achieved by the development of new layer materials and a new disk structure [22, 23]. The first phase-change optical disk product was shipped in 1990 by Matsushita. In 1995, a new concept, the dual function PD disk, arrived on the multimedia scene which system can operate both a CD-ROM and a phase-change optical disk PD [24] and now rewritable CD-RW is following.



Fig. 11. High resolution TEM (Transition electron microscope observation of ZnS (a) and new ZnS-SiO<sub>2</sub> mixture dielectric films (b).

The first version phase-change optical disk product with 4-layer structure showed more than 100,000 overwrite cycle performance. The new 5-layer structure, which has the additional  $SiO_2$  layer shows more than 1,000,000 overwrite cycles. Fig. 12 shows more than 2-million cycle characteristics of the phase-change optical disk with the additional  $SiO_2$  layer.

The sensitivity of the phase-change optical disk was rather low at the first version disk of the laser power of 21mW on the disk. For amorphous mark forming, it needs melting process and the melting temperature of GeTe-Sb<sub>2</sub>Te<sub>3</sub>-Sb active layer materials were around 600 °C, a rather high temperature. But the recording layer thickness was around 20 nm and the heat capacity of the layer was very small. Table 1 shows the optical, thermal and mechanical properties of the phase-change optical disk layers. The heat capacity of the thin active layer (24 nm) of the 1 $\mu$ m<sup>2</sup> mark is roughly calculated as the value of 2.5×10<sup>-5</sup> nJ/ $\mu$ m<sup>2</sup> and the laser spot energy supply is much larger than this value even at 10 mW laser power level irradiation.

The sensitivity of the phase-change optical disk is controlled by the disk layer structure. The reflection metal layer of Al works as the quenching layer of the recording phase-change layer for amorphous mark formation and the upper protection dielectric layer thickness control the cooling rate and also the disk sensitivity.

Material	Refractive		Young's	Poisson's	Specific	Thermal	Coefficient
	index	Density	modulus	ratio	heat	conductivity	of linear
	λ=830nm	(kg/m³)	$(N/m^2)$		(J/(kg ⋅K))	$W/(m \cdot K)$	expansion
GeTe-Sb <sub>2</sub> Te <sub>3</sub> -Sb							
(Amorphous)	4.6+1.0i						
GeTe-Sb <sub>2</sub> Te <sub>3</sub> -Sb							
(Crystal)	5.7+3.0i	6150	$5.49 \times 10^{10}$	0.33	$0.209 \times 10^{3}$	0.581	$1.1 \times 10^{-5}$
2 : 1 : 0.5 (mol ratio)							
ZnS-SiO <sub>2</sub>	2.0	3650	$7.81 \times 10^{10}$	0.2	$0.263 \times 10^{3}$	0.657	7.4×10 <sup>-6</sup>
4 : 1 (mol ratio)							
SiO <sub>2</sub>	1.46	2202	$7.81 \times 10^{10}$	0.2	$0.753 \times 10^{3}$	1.313	5.5×10 <sup>-7</sup>
Al Alloy	2.2+7.5i	2750	$7.03 \times 10^{10}$	0.345	$0.892 \times 10^{3}$	$0.215 \times 10^{3}$	$2.2 \times 10^{-5}$
Polycarbonate	1.58	1200	$2.26 \times 10^{9}$	0.3	$0.126 \times 10^{2}$	0.223	7.0×10 <sup>-5</sup>

Table 1. Optical, mechanical and thermal properties of materials.

Latent Heat (Crystal  $\Leftrightarrow$  Liquid) 0.682×10<sup>5</sup> (J/kg), (Amorphous  $\Leftrightarrow$  Liquid) 0.356×10<sup>5</sup> (J/kg)

For the disk rotation linear velocity of 10 m/s, the cooling rate becomes more than the critical cooling rate of amorphous formation of 3.4 K/ns. We obtained that the overwrite cycle characteristics and the disk sensitivity are not the trade-off relation. Then we developed the high sensitivity PD



phase-change optical disk which has 4-layer structure and more than 500,000 overwrite capability by layer thickness improvement.

Fig. 12. Two million overwrite cycle test results of phase-change optical disk with additional SiO<sub>2</sub> protection layer.



Fig. 13. The sensitivity of phase-change optical disk products O: First version phase-change optical disk (1990), ( $\lambda$ =830nm, NA=0.5, V=12m/s);  $\bullet$ : PD disk (1995), ( $\lambda$ =780 nm, NA=0.5, V=12m/s);  $\Delta$ : Rewritable DVD-RAM (4.7GB), (2000), ( $\lambda$ =650 nm, NA=0.6, V=6 m/s).

Phase-change optical disk sensitivity was improved by the use of a basic 4-layer structure. Fig. 13 shows the overwrite sensitivity characteristics of three phase-change optical disk products. The first version phase-change optical disk needs around 21 mW laser power on the disk (1990).

At that time the sensitivity of MO disk was around 10 mW, but the laser source power was almost the same as for phase-change optical disk drive. Optical transmission efficiency of MO drive was lower than that of the phase-change optical disk drive applying BS (beam splitter) or PBS (polarized beam splitter) in the optical pass.

The sensitivity of PD disk was subsequently improved by decreasing the heat capacitance and cooling rate by the disk layer structure (1995). Then the sensitivity became almost the same for MO and phase-change optical disk.

# 5. Technology comparisons of CD-ROM, phase-change and MO (magneto - optical) disk

Only the optical disk technology has the ROM function other than the HDD technology, which is suitable for multimedia applications.

It has long been a topic of discussion in optical disk memory research and development worlds as to which method best meets multimedia optical disk applications, the magneto-optical (MO) technology or the phase-change optical disk technology.

Table 2 shows comparisons of three technologies: the first is ROM (Read only CD disk), the second is phase-change optical disk and the third is MFM (Magnetic field modulation) recording magneto-optical (MO)disk.

The main advantage of phase-change optical disk technology is that signal reading process is the same as ROM disk. After overcoming the issues such as cycle performance and sensitivity of the phase-change optical disk technology, we proposed a new concept of "PD" system which can play both CD-ROM and rewritable phase-change optical disks in one drive, the same as rewritable CD (CD-RW). Today, rewritable DVD system can operate CD-ROM, DVD-ROM and also rewritable DVD.

Term/ Media	CD Disk	Phase-change Disk	Magneto optical Disk (MFM)		
Read/Write Head	Optical Head	Optical Head	Optical Head & Magnetic Head		
Write Mechanism	Emboss-Pit	Amorphous Mark	Magnetization Domain		
Read Mechanism	Diffraction	Optical Constant Change	Polarization Change		
Signal Detection	Reflectivity	Reflectivity	Kerr Rotation Change		
	Change	Change			
Readout	1.0	1/4	1/80		
Amplitude Signal	(normalized reflectivity)				
Disk Track	λ/4 Emboss-Pit	$\lambda/8$ Pre-Groove	$\lambda/8$ Pre-Groove		
Structure		λ/8 Emboss-Pit	λ/8 Emboss-Pit		
Optical Path	P.B.S	P.B.S	B.S		
	$\lambda/4$ -Plate	$\lambda/4$ -Plate	P.B.S		
			Analyzer		
Disk Materials	Polycarbonate	Polycarbonate	Polycarbonate		
Substrate	Al-alloy	Al-alloy	Al-alloy		
Reflection layer	-	Ge-Te-Sb	Tb-Fe-Co		
Active layer	-	$ZnS-SiO_2$	SiN		
Dielectric layer					
Function	Read-Only	Overwrite	Overwrite		

Table 2. Technology comparison of CD, phase-change and MO disks.

# 6. Thin substrate technology of phase-change optical disk promotes DVD

The general method of high density recording for optical disks is to introduce large numerical aperture (NA) lens to form the smaller laser spot. But the large numerical aperture lens is strongly affected by the disk substrate tilt angle for forming the small spot. We first reported that a thin disk substrate is effective for resolving the disk tilt problem during high density recording. We developed a high density 90 mm diameter phase-change optical disk for an ISO standardization proposal in 1995 [25]. It featured top-level technologies such as a red light laser diode, a large numerical aperture NA (0.6) lens and thin disk substrate (0.6 mm) at that time [26, 27]. Fig. 14 shows the crosstalk characteristics of two types of disks, disk substrate thickness t=1.2 mm and t=0.6 mm when using large numerical aperture lens (NA=0.6). The thin substrate disk of 0.6mm thickness shows lower crosstalk characteristics than the thick substrate disk under conditions of large tilt angle.

The conventional optical disk CD has the capacity of 650 MB and for the next genewration optical disk, the capacity requirement was 4.7 GB for recording 2 hour high quality cinema title. Then, next generation DVD (Digital versatile disk) specifications demand a thin disk substrate (t=0.6 mm), a bonded disk structure, a large numerical aperture lens (NA=0.6) and red laser diode wavelength of 650 nm. A simple overwrite disk function and ROM disk compatibility of the phase-



change optical disk is also featured in the rewritable DVD specifications of DVD-RAMs and DVD-RWs.

Fig. 14. Comparison of the tilt angle dependency of crostalk for substrate thickness of t=1.2 mm and thin substrate of t=0.6 mm. Lens numerical aperture : NA=0.6.



Fig. 15. Optical disk drive market growth.

The disk format life is around 15 years and these years, the new DVD-ROM replaces the conventional CD-ROM market in 2000. Fig. 15 shows the market change of CD-ROM and DVD-ROM drives. Rewritable phase-change CD-RW drive shipment increases these years.

## 7. High density recording technologies of phase-change optical disks

### 7.1. Short wavelength blue laser high density recording

The phase-change recording layer also has the advantages of high signal output and response to a wide spectrum of wavelength. Table 3 shows the wavelength dependency of the complex refractive index of the phase-change material film in the amorphous and crystalline state. Though both the refractive index and the extinction coefficient are decreasing at short wavelength, the difference of the value between amorphous state and crystalline state keeps large. Then the signal output by the reflectivity change is large.

Fig. 16 shows the blue laser recording marks, the track pitch Tp is 0.6  $\mu$ m, land and groove recording marks. The recording density was estimated to be 9 Gbit/in<sup>2</sup>, the laser wavelength was 425nm, the lens numerical aperture was 0.6.

Wavelength	Refractive index		
	Amorphous	Crystal	
830 nm	4.61+1.05i	5.67+3.01i	
780 nm	4.47+1.04i	5.07+3.42i	
650 nm	4.21+1.89i	4.56+4.23i	
430 nm	3.08+2.51i	2.21+3.77i	
405 nm	2.90+2.51i	2.03+3.58i	

Table 3. Wavelength dependency of complex refractive index (N=n+ix\_k) of phase-change material GeTe-Sb $_2$ Te $_3$ -SB film.

Three main approaches have been proposed to increase the recording density of phase-change optical disks. The first is to combine a short wavelength laser with a large NA lens, recently DVR technology is proposed, which is applying larger numerical aperture lens of NA=0.85 and the new disk structure of thin cover-layer, the thickness is 0.1 mm for 0.6 mm disk substrate. This new DVR-blue system shows the recording capacity of 22.4 GB/ side, the disk diameter is 120mm, the laser diode wavelength is 405 nm [28]. The other large numerical aperture recording is SIL (solid immersion lens) recording, the lens numerical aperture is NA=1.5, the recording density is increasing to 45G bit/in<sup>2</sup> by blue laser diode on the phase-change optical disk [29].



Fig. 16. TEM photograph of blue (SHG) laser recording marks. Wavelength = 425 nm, NA = 0.6, MI = 300 nm, Signal: f=6.6 MHz, v=8.2 m/s.

#### 7.2. Dual-layer recording technology

The second approach is dual layer recording, creating volumetric rather than two-dimensional surface recording. The dual layer optical disk DVD is read out from one side, which has been commercialized for 8.5 GB dual layer DVD cinema titles. The phase-change rewritable dual layer optical disk of 8.5 GB technology was announced, which achieves nearly double the previous density [30]. The phase-change optical disk system is composed with laser optical head only other than MO MFM (magnetic field modulation)system, which has two heads, optical head and magnetic head. The phase-change optical disk, optical head only system can record volumetric data by focus position choice in vertical direction and the MO magnetic head system can record data on only media surface. The former achieves increased recording capability by techniques such as multi-layer structures. The dual-layer phase-change optical disk shows a density of 6.4 Gbit/in<sup>2</sup> using a conventional optical system (laser wavelength of  $\lambda$ =650 nm, lens numerical aperture NA=0.6) and disk structure. This technology has the advantage of the feature of enhanced density and compatibility with DVD head.

Fig. 17 shows a cross sectional view of a blue laser dual-layer rewritable phase-change optical disk. The first medium has a high transmission characteristic of around 45% in the crystalline state with a recording reflectivity difference of 7%. The second medium has a high reflectivity characteristic. As a result, the signal output of the second medium becomes  $24 \times 0.5 \times 0.5 = 6\%$  by the absorption of the first medium, which closely matches the value of the first medium [31]. The capacity is increasing to 27 GB.



DVD technology and DVR technology, both can be used to realize dual-layer phase-change optical disk and the combination increases the density more.

Fig. 17. Cross-sectional view of the blue laser dual-layer rewritable phase-change optical disk.

# 7.3. New proposal of MRWM (mark radial width modulation) concept of multi-level recording

The third is the possibility of multi-level recording on phase-change optical disks. Multi-level recording was first announced in a phase-change electrical switching memory (Ovonic memory) device in 1997, which showed 16 switching levels [32]. Multi-level recording, for exemple 4-ary recording gives  $\log_2 4 = 2$  bits per mark, doubling the recording density of conventional binary recording.

The phase-change optical recording layer has a large reflection difference characteristic between the crystalline state (around Rcry = 30%) and the amorphous state (around R = 7%) of the same order as in CD-ROM pit signal output. M. P. O'Neil showed 8-level phase-change recording technology at ODS2000 and announced 2 GB capacity of CD-RW capacity capability [32]. Multi level recording on phase-change media, 4 to 8 level optical recording technologies are announced and the recording density increase is expected around 1.5 to 3 times.

We propose to subdivide this large signal output into multi-level (ML) signals on a phasechange optical disk using the MRWM (mark radial width modulation) method [33].

Binary recording is 2-level: an unchanged state and a changed state, which transalte into 0 and 1. M-ary recording id M-level, giving an unchanged state and multi-amplitude states such as 0, 1, 2, ...(M-1). With level 0 mark unchanged, the mark radial width increases from level 1 to level 3 to deliver 4-level recording.

Fig. 18 shows an outline diagram of MRWM recording marks on a phase-change optical disk. The mark radial widths are 1/3, 2/3 and 1 for level 1, level 2 and level 3 respectively. The assigned laser power is low for level 1 marks but the assigned laser pulse width is long compared to Level 3 marks.



Fig. 18. Outline diagram of MRWM (Mark Radial Width Modulation) 4-level recording on phase-change optical disk.

ML recording requires a high C/N ratio for accurate detection of the M-ary signal. The phasechange optical recording method realizes a greater C/N ratio than the MO disk. Four-level recording gives (0, 1, 2, 3) and gives 4 different states.

Y. Honguh et al. [35] proposed the run-length-limited (RLL) code for multi-level recording introducing the spacing in addition to the minimum and maximum run-length constraints. It showed a magnification factor of 1.76 for (1, 7) code when applied to multi-level recording [34].

The idea of MRWM recording is to assign a specific laser pulse width and power level to a specific mark level. For example, for level 1 mark, since at low laser power, using a long pulse width, the mark length becomes long and becomes the same mark length as Level 3, and increasing the C/N ratio. The minimum mark length of these three levels of marks are designed by the optical head resolution.



Fig. 19. Pulse width and power assigned MRWM recording characteristics of phase-change optical disk. Level 1 (113.3 ns, 6 mW) Level 2 (83.1 ns, 7 mW) Level 3 (45.3 ns, 11 mW)

Signal: f = 6.6 MHz, v = 8.2 m/s.

The assigned laser pulse widths are 114 ns, 84 ns and 46 ns, and the assigned laser power is 6 mW for Level 1,7 mW for Level 2 and 11 mW for Level 3. Fig. 19 shows C/N and amplitude of MRWM recording method with various pulse widths and power conditions. The C/N value is 50.1 dB, 57.5 dB and 61.5 dB for the Level 1, Level 2 and Level 3 marks, respectively. Fig. 20 shows the TEM observation of MRWM recording marks on a phase-change optical disk. The mark radial widths are 200 nm, 400 nm and 600 nm for level 1, level 2 and level 3, respectively.



Fig. 20. TEM observation of MRWM recording marks (Track width: 600 nm) Each marks, Level 1, 2, 3 and the set recording marks (1 to 2), (1 to 3), (2 to 3).

### 8. Combination technology of high density recording

There are two strategies of high density recording of phase-change optical disk, the first is the DVD compatible method which has the optical head, NA = 0.6 and 0.6 mm disk substrate. The second method uses a large numerical aperture head of NA = 0.85 combined with a new disk structure of 0.1 mm transparent overcoat layer.

The recording density increases to double that of a conventional DVD by the ratio of the large numerical aperture lens  $(0.85/0.6)^2 = 2$ . Short wavelength increases the density by the ratio of the wavelength  $(650/405)^2 = 2.6$ .

Rewritable DVD of the 4.7 GB version holds the density of 3.4 Gbit/in<sup>2</sup>. A dual-layer phasechange rewritable disk whose capacity is 8.5 GB has an effective density on one side of 6.4 Gbit/in<sup>2</sup>.

By introducing the magnification factor of the multi-level recording of M = 4 (x1.76), the recording density will further increase. Using the combination with the dual layer technology, the density becomes 30 Gbit/in<sup>2</sup> at 405 nm with an NA = 0.6 lens. This technology also is expected to have the blue laser DVD head compatibility.

Another density increasing strategy is to apply a large numerical aperture lens of NA = 0.85 and a 0.1 mm thin overcoat layer disks for 0.6 mm substrate. The recording density will increase to double and the recording density is predicted to be 60 Gbit/in<sup>2</sup> and the capacity will rise to 83 GB/120 mm/side. By magnifying the multi-level recording from M = 4 to M = 8, the density is expected to increase to more than 100 Gbit/in<sup>2</sup>. Fig. 21 shows the area recording density growth of phase-change optical disks.

J. Tominaga has announced phase-change Super-RENS (super-resolution near-field structure) recording technology, which achieves 13 Gbit/in<sup>2</sup> using the conventional optical head system (laser wavelength = 640 nm, lens numerical aperture NA = 0.6 [35]. The disk structure is composed with additional super-RENS mask layer of AgOx on the bottom dielectric layer. The layer works as the near-field light emission. The super-RENS effect can be combined with the above technologies, resulting in the potential for increasing the density by around 4 times to achieve 240 Gbit/in<sup>2</sup> in the future.



Fig. 21. Areal recording density growth of phase-change optical disk. PD ( $\lambda = 780$  nm, NA = 0.5), 4.7 GB DVD-RAM ( $\lambda = 650$  nm, NA = 0.6), 8.5 GB Dual-layer disk, Blue wavelength 27 GB Dual-layer disk, DVR, SIL (NA = 1.5), Multi-level recording, Super-RENS (640 nm, NA = 0.6).

### 9. Ultra short pulse femto second laser response on phase-change media

Recently, short pulse width laser such as femto to pico second pulse laser have become popular. In high-speed fiber communication, the high-resolution laser processing field and ultra-high-speed time-resolution measurement technology, these femto lasers have achieved ultra-high-speed chemical reactions and bio-molecular dynamics. A 120 fs laser pulse of laser wavelength 800 nm in silicate glass demonstrated a photo-induced refractive index change, which is considered by multiphoton absorption process [36]. Laser processing on the metal or ceramics is done almost in laser ablation process by femto second laser irradiation.

Both are important characteristics, the recording density and the recording data rate. The recording speed on phase-change optical disk is advancing recently from 10 Mbt/s to 100 Mbit/s [36]. It is unknown that the speed limitation of amorphous mark formation and this paper tries to obtain the femto second response of the phase-change films.

Conventional optical disk recording is performed by laser spot irradiation on the rotational disk. In this case, the laser irradiation time on the portion of the disk is around 10 ns to 100 ns, a rather long time compared with the femto second laser spot irradiation. The recording process includes the heat diffusion in the layers. The temperature increasing area is wider than the laserspot size, which means the mark size and the position of the mark are determined by not only the beam factor ( $\lambda$ /NA) but also the disk thermal characteristics and the pulse duration. Heat diffusion of the conventional laser recording limits the performance of future high-density and high-data rate optical disk.

This time I first examined the response of the femto second laser pulse on the phase-change thin media to obtain the features of the ultra short pulse laser recording.

The experimetal condition of the femto laser irradiations were the wavelength  $\lambda = 800$  nm, the pulse width = 120 fs and the lens numerical aperture of NA = 0.95. The sample disk structure is thet polycarbonate substrate/ZnS-SiO<sub>2</sub> 155 nm/ GeSbTe 24 nm/ ZnS-SiO<sub>2</sub> 45 nm/ Air, without reflection layer. The femto laser incident side is the air side. Fig. 22 shows the TEM (transmission electron microscope) observation of the mark formed by the femto second laser exposure (120 fs). The diffraction pattern shows only hallo pattern of amorphous phase and this experiment shows that order to disorder phase-change occurs by one-shot 120 femto second laser pulse. The mark edge is clear without heat diffusion influence.



Fig. 22. TEM observation of amorphous marks formed by femtosecond laser pulse on the phase-change optical disk media.

This experiment shows the amorphous mark recording data rate of phase-change optical disk is expected to be more than T bit/s.

### **10. Conclusion**

Key technologies obtained by materials research and disk structure development have achieved multimedia phase-change rewritable 4.7 GB DVD products. The application of blue laser

light ( $\lambda = 405$  nm), large numerical aperture lens (NA = 0.85), volumetric (dual layer) recording and multilevel recording shows the potential recording density of the phase-change optical disk to exceed 60-100 Gbits/in<sup>2</sup>. Ultra short laser pulse recording experiment shows that even femtosecond pulse (120 fs) forms amorphous mark on the phase-change material film and gives more than 1 Tbit/s data rate capability. The mark shows one of the method to resolve the heat diffusion limitation of the conventional laser recording.

### Reference

- [1] S. R. Ovshinsky, Phys. Rev. Lett., 21, 1450 (1968).
- [2] T. Yoshida, T. Ohta, S. Ohara, Proc. SPIE, 329, 40 (1982).
- [3] M. Terao, N. Nishida, Y. Miyauchi, S. Horigome, T. Kaku, N. Ohta, Proc. SPIE, 659, 105 (1986).
- [4] T. Ohta, T. Nakamura, N. Akahira, T. Yamasita, Japanese patent No. 1668522.
- [5] T. Ohta, K. Inoue, S. Furukawa, T. Akiyama, M. Uchida, S. Nakamura, Electro. & Comun. Technical Research Meeting Rep. CPM 89-84, 41 (1989).
- [6] M. Okuda, H. Naito, T. Matsushita, Proc. Int. Symp. on optical memory, 73 (1991).
- [7] R. Grigorovici, Amorphous and liquid semiconductors, ed. by J. Tauc, Plenum Press, London, chapter 2 (1974).
- [8] J. Cornet, D. Rossier, J. Non-Cryst. Solids, 12, 95 (1973).
- [9] R. Grigorovici, Amorphous and liquid semiconductors, ed. by J. Tauc, Plenum Press, London, 46 (1974).
- [10] J. Feinleib, J. de Neufville, S. C. Moss, S. R. Ovshinsky, Appl. Lett., 18, 254 (1971).
- [11] W. Klemm, G. Frischmuth, Z. anorg. Chem. 218, 249 (1934).
- [12] Y. Maeda, H. Andoh, I. Ikuta, M. Nagai, Y. Katoh, H. Minemura, N. Tsuboi, Y. Satoh, Appl. Phy. Lett., 54, 893 (1989).
- [14] H. Iwasaki, Proc. SPIE, **3109**, 12 (1997).
- [15] N. Yamada, E. Ohno, K. Nishiuchi, N. Akahira, j. Appl. Phys., 69,5, 2849 (1991).
- [16] N. Yamada, E. Ohna, N. Akahira, K. Nishiuchi, K. Nagata, m. Takao, Proc. Int. Symp. on optical memory, 61 (1987).
- [17] M. Suzuki, I. Doi, K. Nishimura, I. Morimoto, K. Mori, Proc. Optical memory Symposium '88, 41 (1988).
- [18] T. Ohta, M. Uchida, K. Yoshioka, K. Inoue, T. Akiyama, S. Furukawa, K. Kotera, S. Nakamura, Proc. SPIE, 1078, 27 (1989).
- [19] G. F. Zhou, H. J. Borg, J. C. N. Rijpers, M. H. R. Lankhorst, J. J. L. Horikx, Proc. SPIE, 4090, 108 (2000).
- [20] M. Horie, T. Ohno, N. Nobukuni, K. Kioyo, T. Hashizume, M. Mizuno, Tech. Digest, ODS2001, MC1, 37 (2001).
- [21] T. Ohta, K. Inoue, S. Furukawa, K. Yoshioka, M. Uchida, S. Nakamura, Electro. & Comun. Technical Research Meeting Rep. CPM90-35, 43 (1990).
- [22] T. Ohta, M. Uchida, K. Yoshioka, K. Inoue, T. Akiyama, S. Furukawa, K. Kotera, S. Nakamura, Proc. SPIE, 1078, 27 (1989).
- [23] T. Ohta, K. Inoue, M. Uchida, K. Yoshioka, T. Akiyama, S. Furukawa, K. Nagata, S. Nakamura, Jpn. J. Appl., Phys. 28, 123 (1989).
- [24] T. Ohta, K. Yoshioka, H. Isomura, T. Akiyama, R. Imanaka, Proc. SPIE, 2514, 302 (1995).
- [25] 1.3 GB 90mm Phase-change optical disk, ISO/IEC JTC, Project 1.23.14760 (19985).
- [26] T. Ohta, K. Inoue, T. Ishida, Y. Gotoh, I. Satoh, Jpn. J. Appl. Phys., 32, 5214 (1993).
- [27] T. Sugaya, T. Taguchi, K. Shimura, K. Taiara, Y. Honguh, H. Satoh, Jpn. J. Appl. Phys., 32, 5402 (1993).
- [28] M. J. Dekker, N. Pfeffer, M. Kuijper, I. P. D. Ubbens, W. M. J. Coene, E. R. Meinders, H. J. Borg, Proc. SPIE 4090, 28 (2000).
- [29] K. Kishima, I. Ichimura, K. Yamamoto, K. Osato, Y. Kuroda, A. Iida, K. Saito, Proc. SPIE, 4090, 50 (2000).

- [30] K. Nagata, K. Nishiuchi, S. Furukawa, N. Yamada, N. Akahira, Jpn. J. Appl. Phys., 38, 1679 (1999).
- [31] T. Akiyama, M. Uno, H. Kitaura, K. Narumi, K. Nishiuchi, N. Yamada, Jpn. J. Appl. Phys., 40, 1598 (2001).
- [32] S. R. Ovshinsky, Proc. The 9<sup>th</sup> Symp. On Phase Change Recording, 44 (1997).
- [33] M. P. O'Neill, T. L. Wong, Tech. Digest ODS 2000, EB2, 170 (2000).
- [34] T. Ohta, K. Nishiuchi, K. Narumi, Y. Kitaoka, H. Ishibashi, N. Yamada, T. Kozaki, Jpn. J. Appl. Phys, **39**, 770 (2000).
- [35] Y. Honguh, T. Murakami, Electron. & Commun. Jpn. Part 3, 77, 85 (1994).
- [36] K. Miura, J. Qiu, H. Inoue, T. Mitsuyu, K. Hirao, Appl. Phys. Lett., 71, 3329 (1997).