Phase-change optical disk and ultra short-pulse laser response for future advancement

Takeo Ohta, Hiroaki Yamamoto

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

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1. Introduction

With the increasing use of multimedia, phase-change rewritable optical disks are becoming more popular due to their CD (compact disk) 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 overwrite function. 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[2]. Rewritable optical disk technology progressed with the race between the magneto-optical (MO) disks and the phase-change rewritable optical disks. This paper describes the capability of high-density recording (over 100 Gbits/in^2) of the phase-change optical disk memory and new proposal of ultra short pulse (femto second laser) response of the phase-change media for future advancement.

2. Phase-change optical disk materials

2.1 Phase-change chalcogenide materials

The rewritable optical memory phenomenon has been found in $Te_{81}Ge_{15}Sb_2S_2$ composition material[3]. This material was modified from a $Te_{85}Ge_{15}$ eutectic composition by adding Sb and S elements. Figure 1 shows the phase diagram of the Ge-Te system[4]. At the eutectic composition, the melting temperature decreases to 375℃. For the eutectic composition, the melting temperature is at a minimum and viscosity is expected to increase. It is thus easy to freeze the bonding structure in the liquid phase through the cooling process. In the next stage, applicable materials that have rather high-speed crystallization characteristics were used. Phase-change materials for over-writing using one laser spot need to have high-speed crystallizing characteristics. Thus, high-speed crystallizing materials such as the In-Se system were discovered[5]. Then Ge-Sb-Te system was proposed[6, 7] and in the GeTe-Sb_2Te_3-Sb system shown in Fig. 2, the material shows nucleation dominant crystallizing characteristics [8]. In this system, Sb controls the crystalline grain size and the crystallization temperature. Figure 2 shows the crystallization temperature of this system, Sb-rich composition increases the crystallization temperature and decreasing the crystalline grain size. Recently, at the ODS (optical data storage conference, Whistler, May 14-17, 2000) crystallizing growth-dominant compositions in the eutectic composition system, such as $Sb_{69}Te_{31}$, were proposed for high density and high data-rate recording[9]. Figure 3 shows the phase diagram of Sb-Te system, the eutectic composition shows rather high melting temperature of 544.5℃. This

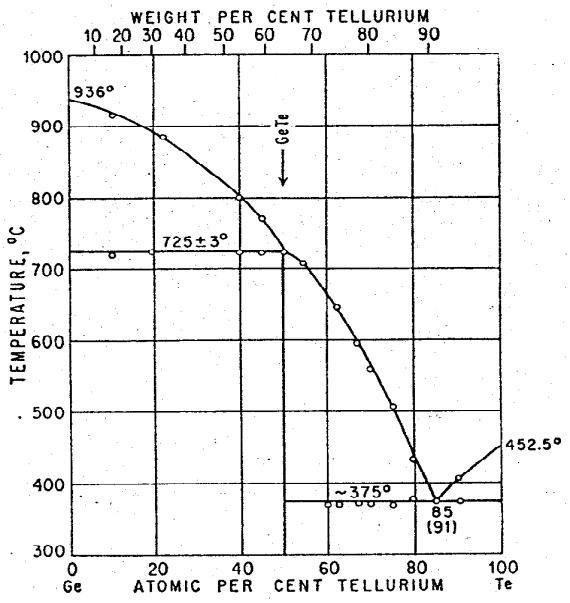


Fig. 1. Phase diagram of Ge-Te system

composition is also plotted in Fig. 2 of GeTe-Sb_2Te_3-Sb system. The melting temperature of Sb is 630℃ and of Te is 449.5℃ respectively. The origin of the growth dominant characteristics of $Sb_{69}Te_{31}$ is now discussed compared the Ge-Te system.

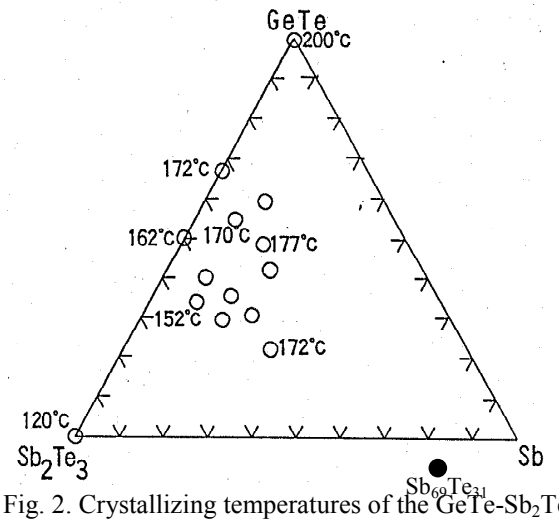


Fig. 2. Crystallizing temperatures of the GeTe-Sb_2Te_3-Sb alloy system

The phase-change processes of the Ge-Sb-Te amorphous material was examined by DSC (differential scanning calorimeter) measurement. It shows that there are two exothermal peaks and one endothermal peak. The first exothermal peak corresponds to the crystallization phase-change and the second to the fcc to hexagonal crystalline structure change. The third peak, the endothermal peak, corresponds to the melt-phase transition[10]. The latent heats of crystalline to liquid (16.3 kcal/kg) and amorphous to liquid (8.5kcal/kg) were obtained from this measurement, the later was calculated as the subtraction value of the exothermic heat from the former value. The model of the phase-change memory is that the reversible transition between the high enthalpy amorphous state and the crystalline state. The complex refractive index N = n + ik of the film is different for the two phases. For example, 2.90 + ix2.51 to 2.03 + ix3.58 from amorphous to crystalline phase-change at the laser wavelength of 405 nm. When the cooling rate is above the critical cooling rate (3.4 K/ns), the portion becomes amorphous phase[11].

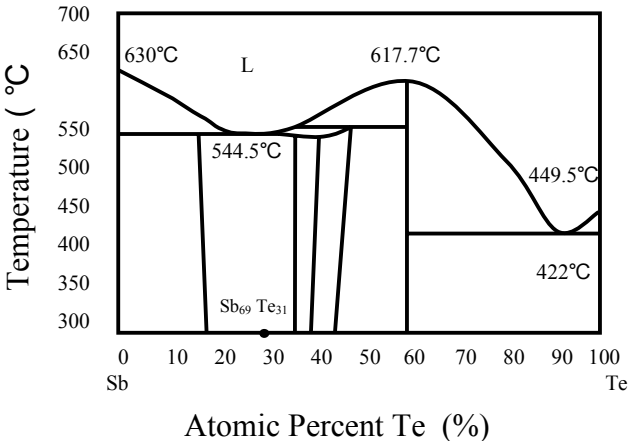


Fig. 3. Phase-diagram of Sb-Te system

3.3 Nitrogen doped GeTe-Sb_2Te_3-Sb active layer

In the phase-change optical disk media development procedure of 1990, we found curious phenomena in the phase-change sample disks. Almost periodically, special disks were sputtered that showed a number of overwrite cycle characteristics almost 10 times larger than the other disks. Our investigation found that these special disks were formed right after the sputtering chamber was cleaned. This means that some adsorbed components in the chamber during the chamber cleaning improved the cycle. Air is comprised of nitrogen, oxygen, some H_2O, and so on. For the chemical stability of the media, we choose nitrogen as a doping component in the active layer. We control the quantity of nitrogen doping by a gas flow ratio of N_2/Ar into the sputtering chamber. The active layer of doped nitrogen shows an N_2 doping dependency of the optical constant (n, k), an increasing N_2 component, and a decreasing refractive index n and extinction coefficient k. This means that nitrogen forms nitride material of M-N in the active layer. M is metal or semi-metal component. Usually, nitride materials show a high melting temperature,

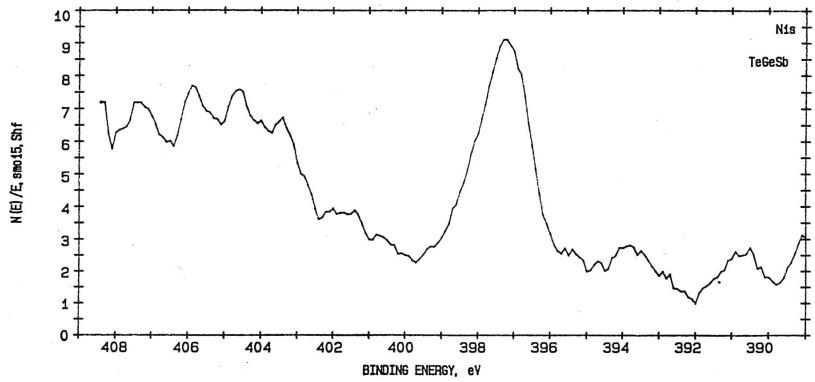


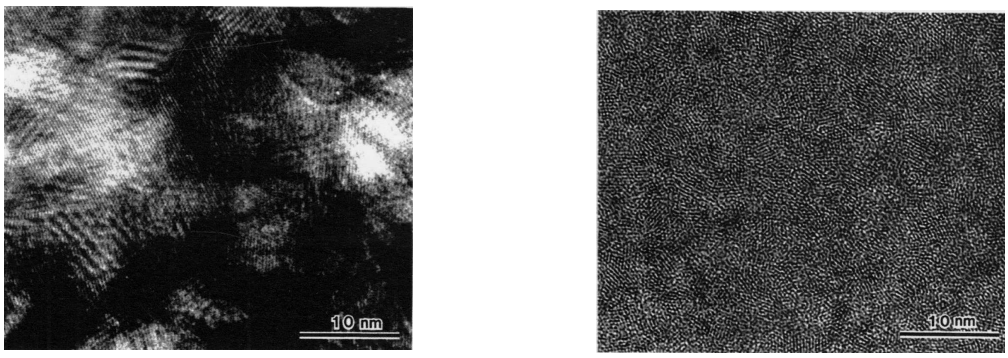
Fig. 4. XPS analysis of GeTe-Sb_2Te_3-Sb film sputtered in N_2/Ar atmosphere. Binding energy of Ge-N : 397.2eV.

which is believed to indicate suppression of the micro-displacement of the active layer components through the overwriting cycle measurement[12].

Figure 4 shows the XPS (x-ray photoelectron spectroscopy) measurement results of the N_2-doped phase-change film. The spectral data shows a large peak at the binding energy of 397.2 eV, which corresponds to Ge-N bonding.

1.2 Thermally-stable new dielectric protection layer

In the early phases of phase-change rewritable optical disk development, the most important subject was cycle degradation. Figure 5 shows a high resolution TEM (transmission electron microscope) image of ZnS and the new ZnS-SiO_2 mixture protection films. The grain size of the ZnS-SiO_2 film is very small, at around 2 nm[13]. The new ZnS-SiO_2 dielectric layer is thermally stable and does not show grain growth, even after annealing at 700℃ (5 min). Grain growth in the ZnS layer was one reason the phase-change optical disks degraded after many rewrites. The first version of the phase-change optical disk product with a 4-layer structure produced a greater than 100,000 overwrite cycle performance.



(a) (b)

Fig. 5. High resolution TEM (Transmission electron microscope observation of ZnS (a) and new ZnS-SiO_2 mixture (b) dielectric film layers.

Figure 6 shows a cross-sectional TEM image of the basic 4-layer structure of a phase-change optical disk of PD(phase-change dual)[14]. The layers comprise a protection layer, a bottom dielectric layer of ZnS-SiO_2 (155 nm), an active layer of GeTe-Sb_2Te_3-Sb (24 nm), an upper dielectric layer of ZnS-SiO_2 (45 nm) and a reflection layer of Al-alloy (100 nm). All the layers are sputter deposited on a polycarbonate disk substrate. These layers work as a multi-layer optical interference structure, controlling disk reflectivity, which is the difference of the reflectivity between the amorphous mark and the crystalline erased state.

One of the cycle degradation model is that 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. After overcoming the cycle issue by key technologies, the phase-change optical disk became a reliable data-recording disk, and its advantage of ROM (read-only memory) disk compatibility, it becomes to be multimedia optical disks such as PD, CD-RW and rewritable DVD. We developed a high-density 90 mm diameter phase-change optical disk for an ISO (International Organization for Standardization) proposal in 1995[15]. This disk featured top-level technologies such as a red light laser diode, a large NA(numerical aperture) (NA=0.6) lens and a thin disk substrate (0.6 mm) [16),17]. A thin disk substrate is effective for resolving the disk tilt problem during high-density recording. A thin disk substrate of 0.6 mm thickness has

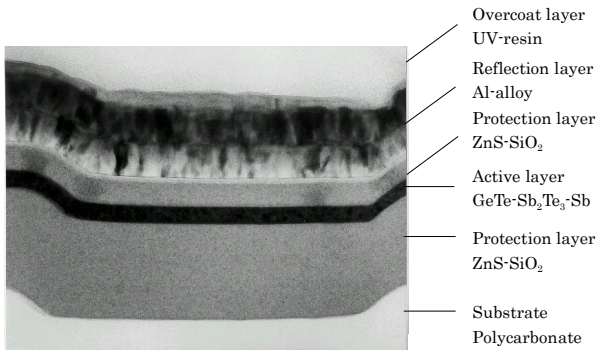


Fig. 6. Cross-sectional TEM observation of the basic 4-layer phase-change optical disk.

lower cross-talk characteristics. These technologies were adapted in the 4.7GB DVD in 1995.

2. The combination of the high-density phase-change optical disk recording

The density of one side of the 4.7 GB version rewritable DVD holds 3.4 Gbit/in^2. A dual-layer phase-change rewritable disk whose capacity is 8.5 GB has an effective density on one side of 6.4 Gbit/in^2, increasing the density 1.9 times[18]. Blue dual-layer disk was announced that the capacity of 27GB and the density of 20.3 Gbit/in[19]. By introducing the magnification factor of the multi-level recording of M = 4 (x1.76) to M = 8, the recording density will further increase approximately 2 to 3 times[20, 21, 22].

Another density increasing strategy is to apply a large numerical aperture lens of NA = 0.85 and a 0.1 mm-thin overcoat layer for 0.6mm substrate[9,23]. The recording density will increase to double that of an equivalent DVD due to the factor of $(0.85/\ 0.60)^2$=2.0. The blue-violet laser wavelength of 405 nm will increase the density to approximately 2.6 times that of the 650 nm laser system of $(650/405)^2$=2.6. The recording density is predicted to be 70 Gbit/in^2 and the capacity will rise to 95GB/120mm/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^2.

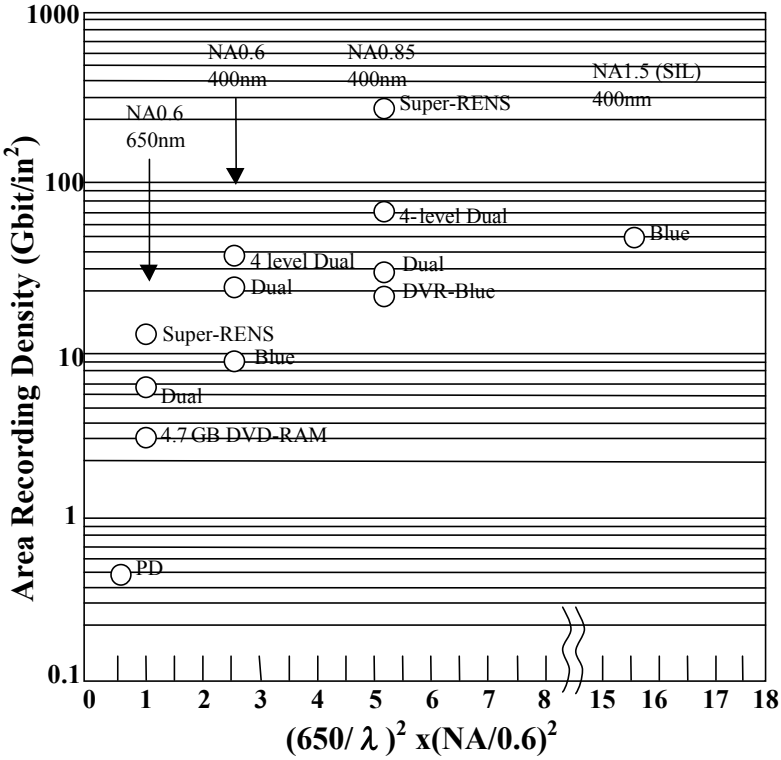


Fig. 7. Area recording density growth of Phase-change optical disk.
PD (λ =780nm, NA=0.5),
4.7GB DVD-RAM(λ =650nm, NA=0.6), 8.5GB Dual-layer disk,
Blue wavelength 27GB Dual –layer disk, DVR, SIL (NA=1.5)
Multi-level recording
Super-RENS(640nm, NA=0.6)

J. Tominaga has announced a phase-change Super-RENS(super-resolution near-field structure) recording technology, which achieves 13 Gbit/in^2 using the conventional optical system (laser wavelength = 640 nm, lens numerical aperture NA = 0.6[24]. The Super-RENS effect can be combined with the above technologies, resulting in a potential density increase of approximately four times to achieve 280 Gbit/in^2 in the future.

Near-Field recording technology is now actively developing, applying SIL(solid immersion lens) technology on phase-change optical disks with GaN blue laser. K. Kishima demonstrated a 45 Gbit/in^2 recording density at ODS2000 [25]. Figure 7 shows the area recording density expansion of the phase-change optical disk with the combination of high density recording technologies.

There are two strategies for the next generation high density phase-change optical disk, the one is DVD compatible strategy which keeps the lens numerical aperture (NA=0.6) optical pick-up and the thin substrate (t=0.6mm) DVD disk structure and combines dual-layer technology and multi-level technologies so on. The other is new disk strategy different from DVD and is introducing larger numerical aperture (NA=0.85) optical pick-up and thin cover-layer (t=0.1mm) disk structure which is not compatible with DVD but can be introduced the technologies, such as dual-layer or multi level recording.

3. Limitations of the conventional laser recording

3.1 Heat diffusion phenomena

Figure 8 shows the thermal simulation results of the temperature distribution in the cross-sectional view of the first version phase-change optical disk. The temperature distribution is calculated after the 30 ns laser-spot irradiation on the rotational disk. The linear velocity is V = 8 m/s, the laser wavelength is 830 nm and the lens numerical aperture is 0.53. It shows that the temperature rising area is wider than the spot size of 0.76 μm (FWHM)(full width half maximum) caused by the thermal diffusion in 30 ns[26]. The temperature distribution profile is asymmetrical between the forward area and the backward area because of the thermal diffusion process.

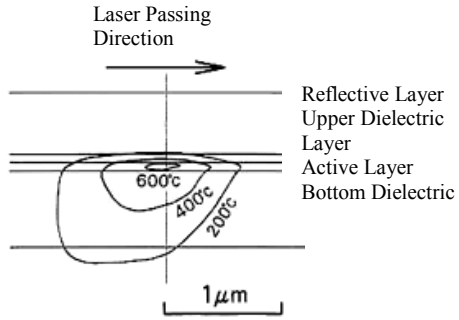


Fig. 8. Cross-sectional view of the temperature distribution of the phase-change optical disk at 30ns laser spot scan.

Thermal diffusion phenomena also affects the thermal deformation of the disk layers. Thermal expansion coefficients of the dielectric materials of SiO_2 and ZnS-SiO_2 are 5.5×10^{-7} and 6.1×10^{-6}, respectively. We compared the thermal deformations of the first version disk structure and new disk structure. Figure 9(a), (b) shows the simulation results of the thickness change of the layers by thermal expansion as the temperature distribution simulation.. All layers show that the thermal expansion and thickness changes are several sub-nm. These deformations are considered the motivating force of the micro-displacement of the active layer components. Figure 9(a) shows the thickness change of the first version disk structure. Figure 9(b) shows the thickness change of the new disk layer structure. When the SiO_2 layer for the ZnS-SiO_2 layer is introduced to the upper dielectric layer, the thickness change of the upper dielectric layer becomes negligible small, compared the value of ZnS-SiO_2 of 0.04nm[26]. The new disk structure, which has a SiO_2 upper dielectric layer, produces more than 1,000,000 overwrite cycles. The Error bit counts, C/N ratio, Erase ratio and Jitter (window % for 10^{-4}bit error rate) are almost stable through the test.

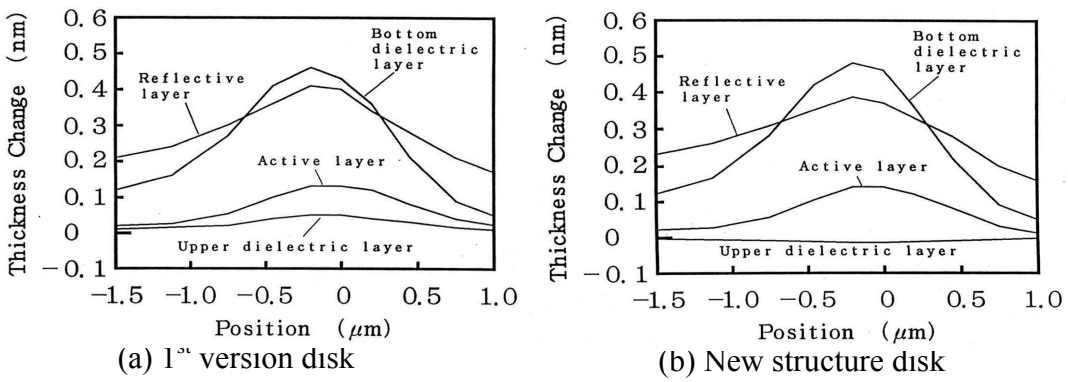


Fig. 9. Distribution of the thickness changes of the disk layers by thermal expansion.
1st version disk (a) : substrate / DL, 160nm / AL, 20nm / DL, 35nm / RL, 130nm
DL : ZnS-SiO_2 , AL : GeTe-Sb_2Te_3-Sb, RL : Al-alloy
New disk (b) : upper DL is replaced by SiO_2 (35nm)
Horizontal axis : laser passing direction, Zero position : center of the laser spot

A conventional laser recording using rather long pulse widths of 10 ns to 60 ns (10^{-9}s) shows large thermal diffusion phenomena in the disk. The pulse means that the irradiation time of a laser spot at a certain point on the rotational disk, and is the time the laser spot takes to go through the point. A short pulse width, such as a femto second (10^{-15}s), will be expected to suppress the thermal diffusion phenomena extremely. The interaction effect of the femto second laser pulse on phase-change films will be discussed later in this paper.

3.2 Model of the recording limitations

Recently, high-density recording technologies applying a large numerical aperture lens, the SIL, the blue laser short wavelength, and so on, have been introduced. These technologies display the following characteristics: the mark size becomes around 100 nm[25]; the high density and high data rate for example, 120Mbps[27]. The width of the area out of the spot size (FWHM) that is heated up by heat diffusion is the so-called dead space. The density becomes higher and the data rate becomes faster, the space of the marks becomes shorter and the time interval of the marks also becomes shorter. Then the dead space and the mark position variation influences the recording density and Jitter performance more strongly.

The area where the temperature is increasing is wider than the laser spot irradiation by thermal diffusion phenomena. Figure 8 and 9 shows the the heated area is wider than the spot diameter of 0.76um(FWHM). Figure 10 shows the model of the limitations of the conventional laser recording.

Laser spot recording is usually a heat-mode recording; the recording layer absorbs the laser light energy and the temperature increases beyond the threshold temperature. For example, the threshold temperatures are the melting temperature for phase-change material (Tm=600°C), the Curie temperature of the Magneto-Optical media (Tc = 200°C), the decomposing temperature of the recordable Dye media (Td=350°C), and so on.

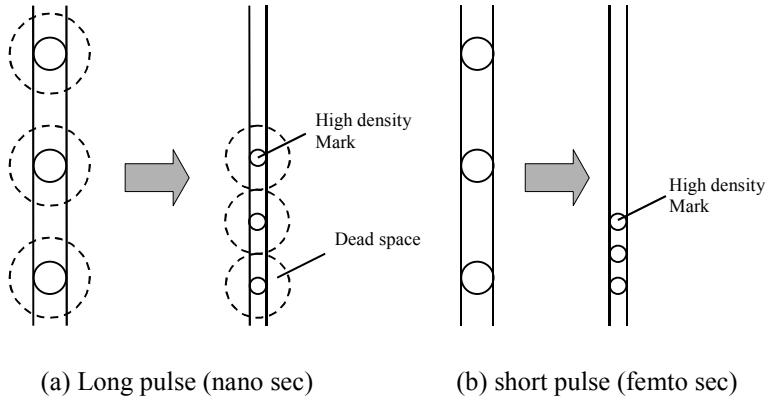


Fig. 10. Concept of the dead space produced by thermal diffusion:
(a) Large heat diffusion by long pulse laser recording
(b) Small heat diffusion by short pulse laser recording

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 temperature increasing area is wider than the laser spot size, which means that the mark size and the position of the mark are determined by not only the beam factor (λ/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 optical disks.

3.3 Femto second laser recording mark and discussions

Recently, short pulse width lasers such as the 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 multi-photon absorption process [28]. The threshold recording power density was 120 nJ/ μ m^2. The dynamics of the magnetization of the MO films were monitored by the femto second laser[29].

Figure 11 (a) shows the TEM observation of the mark of the conventional several-tens nanosecond long pulse-width laser exposure (50 ns) on the rotational disk and (b) shows the mark formed by the femto second laser exposure (120 fs). The conditions of the conventional recording; the lens numerical aperture was NA = 0.5, the laser wavelength was λ= 780 nm, and the recording power was 11 mW. The marks are amorphous and surrounded by a large crystalline band edge. The most significant difference between the mark formed by the femto second pulse laser and the marks formed by the conventional several-tens nanosecond pulse laser is the mark edge figure. The conventional pulse forms intermediate space between the amorphous mark and the crystalline background dead space of 160 nm. The femto second pulse forms an amorphous mark without the crystalline edge band[30]. The intermediate space is a large-grain size crystalline state that is formed by the recording laser spot when melted and re-crystallized in the cooling step. The recording energy density of the femto second mark of the phase-change media was smaller than 1nJ/μm^2, and the conventional disk recording energy density was approximately 2nJ/μm^2.

The conventional laser disk recording process has three stages. The first is a laser spot exposure and the energy absorption, the second is heat diffusion outside of the laser spot, and the third is cooling after the laser exposure time, from 10 ns to 100 ns, depending on the laser spot diameter and the disk rotational speed. The conventional laser recording limit appears in the

second and third process, and comes from the thermal diffusion process. The mark dead space out of the laser spot and the variation of the mark position are caused by the thermal diffusion from a rather long pulse-laser irradiation.

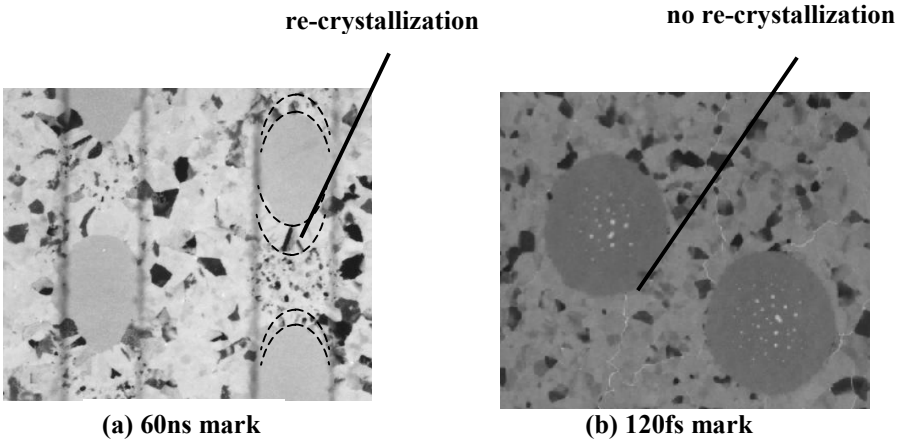


Fig. 11. TEM observation of the amorphous marks on phase-change optical disk.
(a) Conventional laser recording : λ =780nm, NA=0.5, t=60ns, (with a reflection layer)
(b) Femto second pulse laser recording : λ =800nm, NA=0.95, t=120fs, (without a reflection layer)

The femto second laser pulse irradiation is quite different from the conventional laser recording because the thermal diffusion is limited in the fs to ps order, the mark is accurately formed in the laser spot, and the variation of the mark position is negligible without thermal diffusion variation. The short pulse width of 120 fs recording on the phase-change media indicates a high-recording data rate capability of more than 1 Tbit/s. Overwrite process needs ultra high speed crystallizing characteristics and now investigations start for this new material area.

4. Conclusion

Key technologies obtained by materials research and disk structure development have achieved multimedia rewritable 4.7 GB DVD products. The application of blue laser light and volumetric (dual layer) recording have the potential to increase the recording density to 20.3 Gbit/in^2 with an NA = 0.6 lens. The phase-change optical disk has multi-level high-density recording capability. A multi-level recording method and an NA of 0.85 in combination with other technologies indicates the potential for the recording density of the phase-change optical disk to exceed 100 Gbits/in^2 . Ultra-short pulse femto second laser recording on phase-change media is one candidate for a breakthrough of the laser thermal recording limit.

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