

Review

## Development of New Thin Film Multilayered Systems for Recordable Optical Disc Memory Compatible with CD and DVD

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### Abstract

Archival data on the CD-R, which has been explosively popularized in the past five years, cannot be read with DVD-ROM drives or upcoming Blu-ray disc drives if these drives are equipped with a single laser of 650 nm or 405 nm in wavelength. To overcome this inconvenience inevitable in the near future, we developed a new class of recordable optical disc memories in collaboration with DENSO Corporation. The research activities reviewed here involve (1) proposal of a new recording mechanism, (2) observation of transient phenomena in the new recording mechanism, (3) materials design of thin-film multilayered systems, (4)

optimal pre-groove design of optical disc substrates, whose details are described in the research reports in this special issue. The newly developed recordable optical discs were compatible with the conventional CD-R and could be also played with DVD-ROM drives, unlike conventional CD-R. Taking advantage of this first realization of DVD-compatibility, the new medium has already been used in software development for car navigation systems via built-in DVD-ROM drives. This "future compatibility", being an essential requisite for archival purposes, should see numerous applications of various types and shapes.

#### Keywords

Optical disc memory, Combinatorial chemistry, Exothermic reaction, Eutectic alloy, Car navigation systems with a DVD-ROM drive, Needs of the time, MPEG1, Thermal dissipation, Compatibility, Transient phenomena

## 1. Introduction

Information storage is one of the key activities which distinguish mankind from other species. Extensive efforts have been done to explore new ways of information storage throughout the human history. In this special issue, we would like to report an additional "one small step for ... mankind" taken in our laboratory TCRDL in collaboration with DENSO Corporation.

In any applications of information storage, people use essentially three different types of media classified by their functions. One can find a typical example of this in a school class such as a textbook as a read-only-memory; a blackboard as an erasable/rewritable memory; and a notebook as a write-once type memory, to which information is added day after day. This is also the case for optical disc memories of ROM(read only), RW(rewritable) and R(write-once) types.

Optical disc memories are also classified into three families by their capacities: widely used CD(Compact Disc)-family(570-700 MB), DVD (Digital Versatile Disc)-family(2.6-4.7 GB) which is gaining popularity now, and "Blu-ray Disc"-family (25-50 GB), whose RW-type disc is just coming up onto the market. The difference in capacity in the same 120 mm diameter disc comes mainly from the difference in the wavelength of the laser used in the optical pickup such as 780 nm for CD, 650 nm for DVD and 405 nm for "Blu-ray Disc".

If we put the upcoming "Blu-ray Disc" aside, we have heretofore six major versions of optical disc memories: CD-ROM, CD-RW, CD-R, DVD-ROM, DVD-RW and DVD-R. Here, it should be noted that DVD-R is used in this issue to represent DVD+R and DVD-R, and DVD-RW to represent DVD+RW, DVD-RAM and DVD-RW on the market.

A ROM-type disc basically comprises a polycarbonate substrate, a sputter-coated aluminum reflector layer on the substrate, and a spin-coated and UV-hardened protective lacquer layer under a label. The recording pits are directly stamped on substrates in an injection-molding process at the manufacturer. Users cannot erase the data nor record additional data. CD-ROM and DVD-ROM have high reflectance for a wide wavelength range,

reflecting the optical properties of aluminum.

The CD-ROM is the most suitable disc media for mass-distribution of stored information because it can be mass-produced at a very low cost, and played with almost all personal computer.

As for R-type discs, users record data by themselves on discs that are initially blank. Users cannot record data twice on the same position of a disc nor erase them. The CD-R and DVD-R have basically the same recording capacities as the CD-ROM and DVD-ROM, respectively. Using appropriate drives, users can record additional data on a blank area of a CD-R next to the previously recorded area (track-at-once recording mode). As for the DVD-R, so far, the disc-at-once recording mode in which users can record data only once, irrespective of the data size to be recorded, is a kind of de facto standard and the track-at-once recording mode is available only in limited cases.

Blank CD-Rs or DVD-Rs basically comprise a substrate which has a pre-groove for tracking, a spin-coated organic dye layer on the substrate which is sensitive to a laser-light of a specific wavelength range, a sputter-coated gold or silver reflector layer on the organic dye layer, and a spin-coated lacquer layer under a label. Recording pits are formed by the deformation of a metal reflector layer caused by decomposition of the dye layer by an intense laser irradiation. Since CD-Rs and DVD-Rs employ organic dyes with their optical absorption spectra specially tuned for laser diodes of 780 nm and 650 nm, respectively, they have very narrow wavelength windows of high reflectance.

As for RW-type discs, users record data by themselves on initially blank discs, just as with R-type discs. However, users can record and erase data more than 1000 times on the same position of the disc.

Blank CD-RWs or DVD-RWs basically comprise a substrate which has pre-grooves for tracking, a sputter-coated recording layer of a so-called phase-change material, sputter-coated dielectric layers on both sides of the recording layer for protection of the recording layer from oxidation, a sputter-coated metallic reflector layer, and a spin-coated lacquer layer. The optical reflectance of the phase-change material is different between the crystalline phase

and the amorphous phase in a specific wavelength range. The blank area of the recording layer has been made into crystalline phase by laser-irradiation at an intermediate intensity beforehand. The recording pits are formed by changing the recording layer from crystalline to amorphous phase by irradiation of an intense laser shot followed by rapid cooling. The recording pits can be erased by recrystallization.

The reflectance of RW-type discs shows intermediate dependence on the wavelength between ROM-type discs and R-type discs. This is mainly attributed to optical interference in the multilayered structure and the optical property of the phase-change material.

The price of CD-Rs is currently somewhere around ¥70/disc and that for DVD-Rs is ¥250-¥580/disc, whereas that for CD-RWs is around ¥170-¥300/disc and that for DVD-RWs is around ¥650-¥980/disc. As for R-type discs, the spin-coating and drying processes of the organic dye layer are time consuming and are liable to yield defective products, pushing up the production cost. This is especially serious for DVDs, which have finer grooves. In RW-type discs the cost for the initial crystallization seems to be significant as well as the high initial cost for the multi-source sputter-coater.

## 2. Technological background and needs of the time

Prior to discussing the main topic of the present special issue, our previous development of RW-type disc shall be presented as the technological background.

### 2.1 Development of RW-type disc that is compatible with the CD-ROM drive

The first generation CD-ROM drives require optical discs to have a reflectance above 65 % and a modulation (relative change of reflectance) above 60 %. These requisites are satisfied by both the CD-ROM and the CD-R, but not by CD-RW because of the nature of phase-change materials, such as AgInSbTe and  $\text{Ge}_2\text{Sb}_2\text{Te}_5$ .

Three approaches have been taken in pursuing a solution to this problem. The first approach was to increase the reflectance of the RW-type disc at the 780-nm wavelength. However, increasing the

reflectance decreases the absorbance of the laser light, and hence a higher laser power is needed in order to induce a phase change at 780 nm. To overcome the problem associated with this trade-off relationship, Kawai et al. of DENSO Corp. proposed a new "Write at 685 nm (or 830 nm) and Read at 780 nm" scheme.<sup>1)</sup> They inserted additional optical interference layers into the conventional phase change disc structure to obtain higher reflectance at 780 nm and higher absorption at 680 nm. However, even this disc could not attain high modulation so far as the conventional stoichiometric compound  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  was employed.

Therefore, in collaboration with DENSO, we (TCRDL) studied the dependence of optical constants and microstructures of thin films of the compositions along the pseudo-binary GeTe-Sb<sub>2</sub>Te<sub>3</sub> line on the GeSbTe ternary phase diagram to determine the optimal composition for a CD-RW disc with high modulation that would be compatible with a conventional CD-ROM drive. A "combinatorial-chemistry approach" using two sputtering targets: GeTe and Sb<sub>2</sub>Te<sub>3</sub> led us to find the best composition  $\text{Ge}_{39}\text{Sb}_{10}\text{Te}_{51}$ . The new disc attained 65 % reflectance and 60 % modulation.<sup>2)</sup>

The second approach was to break away from the CD-family and propose a different scheme of drive systems and different RW-type 120 mm disc-in-a-cartridge media such as MO or the Panasonic "PD". However, it seems that these RW-type discs have not been successful so far in popularization since they are not compatible with the prevalent conventional CD-ROM drives.

The third approach promoted the production of the second generation CD-ROM drive equipped with an auto-gain controller to read rewritable discs based on the phase-change material of AgInSbTe with 20 % reflectance. Although the first approach could supply a rewritable disc which can be read by first-generation CD-ROM drives, the rapid growth of the personal computer market has made the first-generation CD-ROM drives to be a minority, and so the third approach seems to survive so far. This situation typically illustrates the conflict between material research and system integration technology as frequently seen at every corner of technological development.

However, the needs of the time seem to have selected finally not the CD-RW but the CD-R for explosive popularization.

## 2. 2 The needs of the time: explosive popularization of the CD-R

Although the CD-RW covers all of the functions of the CD-R, the CD-R has been more popularly used than the CD-RW. Since the revision of a data file can be done on the hard disc and the revised file is then saved on removable media, rewritability is not a key requisite for removable media. It is also convincing from another point of view if one is reminded that most of VHS video tapes are used for recording only once irrespective of its rewritable nature. With CD-R, people can easily exchange digital information of the capacity larger than 1.44 MB of a floppy disc at a lower cost than with CD-RW and can read it with prevalent CD-ROM drives. For archiving purposes which has been the most essential function in the history of data storage, the inerasability of the CD-R has not been a demerit but rather a merit. After 1997, CD-R production has shown a remarkable increase, and has got a very large market as a blank storage medium, as shown in Fig. 1.<sup>3)</sup>

## 2. 3 Inconvenience around CD-R

DVD-ROM drives can play DVD-ROMs and DVD-Rs. Playing CD-ROMs is also a prerequisite of DVD-ROM drives. Since the CD-ROM has enough reflectance at 650 nm, it can be played by

DVD-ROM drives. To play CD-Rs, an additional 780-nm laser diode is necessary, which pushes up the price of drives.

DVD-ROM drives are now coming into widespread use. In this situation, the fact that the CD-R cannot be played with DVD-ROM drives with a single 650 nm-laser diode will become a serious inconvenience when major optical disc drives employ laser diodes of 650 nm or 405 nm in the near future.

This is a critical contradiction to archiving purposes for the CD-R. For example, a memorial photograph is no longer a memorial photograph if it is archived into an optical disc at 780 nm and cannot be read at 650 nm. Apparently, in transient years, manufacturers of optical disc drives cannot disregard this users' inconvenience because the CD-R market has been fully extended, and manufacturers will take a policy to produce DVD-drives having two laser diodes of 780 nm and 650 nm to read CD-R, sacrificing the cost and compactness of the drive.

As a matter of course, this policy will not hold permanently for example after "Blu-ray Discs" become popular, to make such drives with three laser diodes for 780 nm, 650 nm and 405 nm from the view point of cost. Thus, the above-mentioned inconvenience is inevitable. Therefore, needs for a new CD-R that is compatible with the DVD and the "Blu-ray Disc" is quite natural from the viewpoint of technical trends.

## 2. 4 Special circumstance in automobile use

In automobile use, compactness, durability and cost-reduction are requested with more emphasis than in home- or office-use. When car navigation systems with a DVD-ROM drive (hereinafter referred to as DVD-navi) came on the market in the late 1990s, it was difficult to employ a 780 nm-laser diode in addition to the 650 nm-laser diode. Therefore, the above-mentioned inconvenience was not a future problem. DVD-navi software developed and improved with engineering workstations had to be tested in DVD-navi daily and hourly. Since DVD-navi could read maps on DVD-ROMs and could play audio CDs, but could not read conventional CD-Rs, only DVD-Rs could be used for exchanging the several to several ten MB DVD-

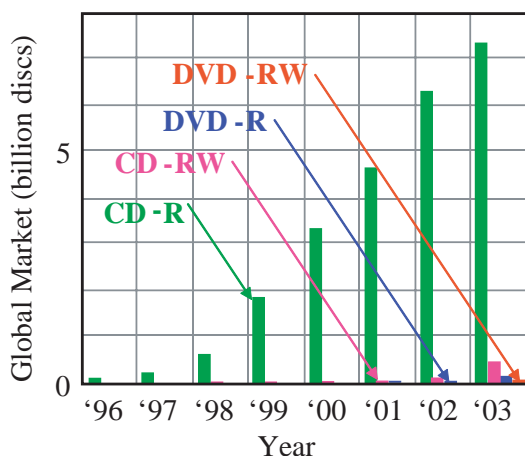


Fig. 1 Growth of global market of optical disc media. (Data by JRIA<sup>3)</sup>)

navi programs between workstations and DVD-navis. Here, it was very wasteful to use DVD-Rs only once based on disc-at-once mode, irrespective of the huge GB capacity and considerable cost of DVD-Rs.

### 3. Concepts and key technologies of the newly developed optical memory

To get rid of the above-mentioned inconvenience around CD-R, we have tried to develop an alternative new class of write-once type optical disc memory, on which data can be recorded with conventional CD-Recorders and can be played at wavelengths of 780 nm, 650 nm and possibly at 405 nm for "Blu-ray Discs", as is the case for the CD-ROM. Recently, we have got a success in realizing this new disc memory, which we have named the "CD-Rc" after "recordable optical disc memory compatible with CD and DVD".

#### 3.1 Guiding principles of the development

The guiding principle of our development of the recording layer for the CD-Rc is the utilization of interlayer exothermic chemical reactions between a transparent inorganic dielectric layer and an adjacent metal reflector layer triggered by the recording laser irradiation and maintained by the exothermic heat of reaction. The reaction ruins both the transparency of the dielectric layer and the reflectivity of the metal reflector layer, resulting in the formation of recording pits with low reflectance and high modulation. To our knowledge, there had been no proposal to utilize the metal reflector layer itself for laser-induced interfacial reaction to form pits. This guiding principle had been introduced based on our previous experimental experience on unexpected low reflection caused by coloration or degeneration in thin film metal/insulator systems.<sup>4)</sup> A gentle and monotonic change in reflectance and recording sensitivity in a very wide wavelength range are expected under this guiding principle based on inorganic materials.

To form recording pits it is necessary to increase the temperature of the interface of the two layers beyond the threshold temperature to start the chemical reaction. To get high recording sensitivity, that is, to attain this threshold temperature with a lower laser power, it is important to reduce thermal

dissipation. Decreasing the reflector layer thickness reduces thermal dissipation but simultaneously decreases the optical reflectance. Therefore, metals with high reflectance and low thermal conductivity are strongly recommended for the reflector layer. However, the physics of metals teaches that high free electron density causes high reflectance and simultaneously high thermal conductance. Thus, recording sensitivity and reflectance seems to be fatalistically in a trade-off relation.

#### 3.2 Key breakthroughs of this development

We could get rid of this trade-off relation by utilizing the fact that thermal conductivity of not a few metals decreases as much as 50 % when they melt. We selected a metallic material with high reflectance and low melting temperature so that it melts by recording laser irradiation. Thus thermal dissipation was reduced and the recording layer was heated to higher temperature resulting in high recording sensitivity.

Furthermore, the melting of the metal reflector layer promotes the reaction to attain a higher recording speed. We observed this by the specially designed apparatus described in the second research report of this special issue. By inserting a thin blocking layer between the transparent inorganic dielectric layer and the metal reflector layer, spontaneous reactions without laser irradiation were subdued to pass the durability test of 70°C, 50 %R.H., 96 hrs. The concrete description of the development of the recording layer materials for the CD-Rc is given in the first and the third research reports in this special issue.

Besides the above-mentioned development of the recording layer materials, the development of a new shape of pre-groove on the substrate for tracking was also necessary in order for CD-Rc to be played with both CD-ROM drives and DVD-ROM drives. We theoretically and experimentally derived the best shape of the pre-groove of CD-Rc which was shallower and narrower than that of the conventional CD-R, as described in the fourth research report in this special issue.

CD-Rcs can be formed by sputter-deposition process which is fully established as a low-cost and high-throughput process in conventional production lines of CD-RW and DVD-RW, and yet we can do

without Te, which is used in CD-RW and DVD-RW. By getting out of time-consuming spin-coating and drying processes of the dye layer, we can also eliminate the harmful waste of organic dye solvent.

It was confirmed that an audio DVD player which could not play a commercially available CD-R could play CD-Rc. Video images recorded on CD-Rc discs from VHS video-tapes using an MPEG1 board could also be run smoothly on personal computers via almost all CD-ROM drives. There were several CD-ROM drive products which could not run CD-Rc smoothly as sometimes experienced in commercially available CD-R discs.

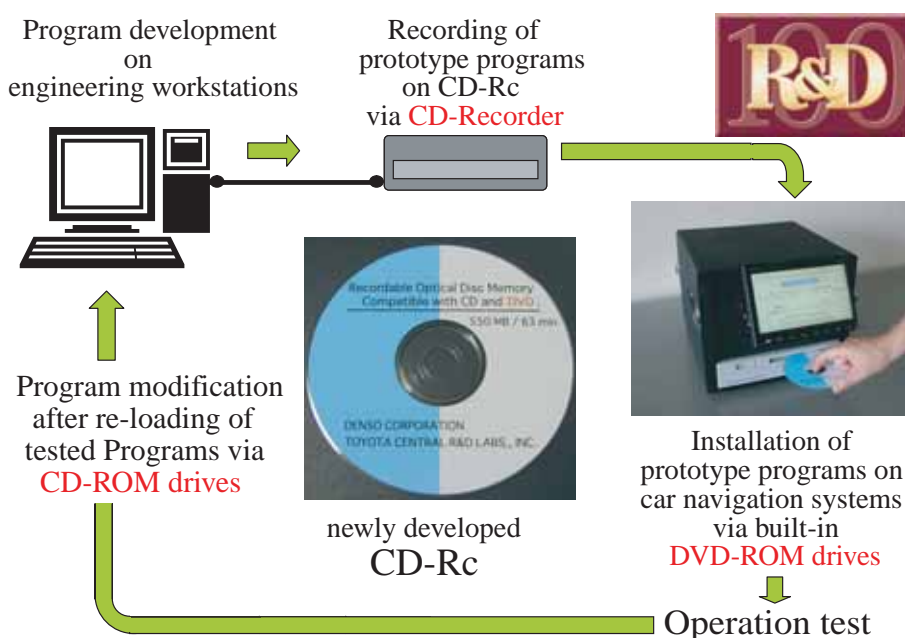
#### 4. Practical application

The CD-Rc has been utilized daily and hourly in the development of DVD-navi software. In the development of DVD-navi software, prototype programs had to be installed on Flash-ROMs in DVD-navi to be tested for functioning correctly. An alternative way to avoid the wasteful and costly usage of DVD-R for the purpose mentioned above in 2. 4 was to modify the system to be connected to a

CD-ROM drive. A new program is recorded on CD-R and was installed into the Flash-ROM via this CD-ROM drive. In this way, we could use a commercially available CD-R, however, another inconvenience sprang up; tentative cumbersome modifications of the DVD-navi by removing the outer case, connecting wires and modifying the electronics had to be done for a number of DVD-navis used for testing the programs and for every new model.

Therefore we provided CD-Rcs for the development of DVD-navi software. It was confirmed that the CD-Rc could be actually played with DVD-navi. The use of CD-Rc offered the simplest method for installing a new program, that is, a new program is recorded on CD-Rc and is installed into a Flash-ROM by running the CD-Rc in DVD-navi, as shown in **Fig. 2**.

Since this was the first realization of DVD-compatible CD-R and also the first practical use of data exchange between the CD-Recorder and the DVD-ROM drive with a single optical pickup of wavelength 650 nm, the CD-Rc was awarded 38th



**Fig. 2** The first practical application of CD-DVD compatibility of CD-Rc in the software development for car navigation systems. For this firstly attained compatibility, CD-Rc was given 38th Annual R&D100 Award in 2000<sup>5)</sup>.

annual R&D 100 Awards in 2000.<sup>5, 6)</sup>

## 5. Conclusion

Based on a new recording concept, we have developed a new write-once type disc, the CD-Rc, which has attained compatibility between CD-Recorders and DVD-ROM drives for the first time. The production of the CD-Rc does not yield waste of organic solvent for dye, as do conventional R-type discs, and does not use sputtering targets containing Te, as do RW-type discs. Lower production costs than CD-R or CD-RW can be expected.

However, the development of storage media is a typical examples of the conflicts between material research and system integration technology as was seen in our previous CD-compatible CD-RW development as described above in **2. 1**. It is not easy for new materials to come into widespread use.

Now the RW-type disc in "Blu-ray Disc"-family is about to emerge on the market. Recording materials for R-type discs for this family are still in the argument. Organic dye is not useful in this wavelength range because of deterioration by reading laser light. Several material systems including phase-change types and the interface reaction types, as presented here, are on the list of candidates for recording layers in the optical disc memory community.

So far, the CD-Rc has been utilized daily and hourly for the development of DVD-navi software. The concept and materials system can be widely used in various types of storage media for "future-compatible" archiving purposes besides optical discs.

It is interesting to recollect that the Rosetta Stone was future compatible because it was written in three languages: using hieroglyphs, demotic and Greek alphabets, just as CD-Rc which is future compatible because it can be read at three wavelengths 780 nm for CD, 650 nm for DVD and possibly 405 nm for the "Blu-ray Disc". The concept introduced in CD-Rc will hopefully be another "Rosetta stone", triggering a new era of future-compatible write-once memories of various types and shapes.

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## References

- 1) Kawai, S. : Unexamined Patent Pub., H5-205316 (1993) (in Japanese)  
Kawai, S. : Examined Patent Pub., P320615 (2001) (in Japanese)
- 2) Kato, N., Takeda, Y., Fukano, T. and Motohiro, T., Kawai, S. and Kuno, H. : "Compositional Dependence of Optical Constants and Microstructures of GeSbTe Thin Films for Compact-Disc-Rewritable (CD-RW) Readable with Conventional CD-ROM Drives", Jpn. J. Appl. Phys. Pt.1, **38**-3B(1999), 1707-1708
- 3) JRIA (Jpn. Recording-Media Ind. Assoc.) : "Press Releases Nov. 25, 2002, Another Quantum Leap for Recordable DVDs Forecasts for Recording Media in 2003 Global Demand and Production", JRIA, (on line), available from <<http://www.jria.org/english/maain.html>>, (accessed 2003-07-18)
- 4) Motohiro, T. and Taga, Y. : "Elliptical blue patches growing in obliquely deposited WO<sub>3</sub> films", Thin Solid Films, **172**(1989), L71-L75
- 5) "Optical Disc More Compatible", R&D Magazine, **42**-9(2000), 118
- 6) DENSO Tech. Rev., **6**-1(2001), 121

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