

# Research Progress on High-Density Optical Storage Materials for Blue-Green Laser Recording

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The key for the development of high-density optical storage technology nowadays is to develop short wavelength (blue-green laser) recording media and devices. Based on the progress achieved in the key program of National Natural Science Foundation of China "high-density optical storage materials using blue-green laser recording", the chemical composition, microstructure, storage performance and related mechanisms of some kinds of novel high density optical storage materials are presented in this paper. The research method and clue for super high-density optical storage materials and technologies are highlighted.

**Key words** high-density optical storage, optical disk, blue-green laser, optical storage material

Information technology and industry are key events in the 21<sup>st</sup> century. Information storage technology becomes one of the most important parts in information technology. A technology revolution has been started up in the information storage field with increasingly high demands for storage capacity at the dawn of a full-scale multimedia and internet age.

Optical storage technology is a newly developed

information storage technology after the emergence of magnetic storage. Recently, not only in the R & D, but also in the market, great progress has been obtained in this field. Optical disk products are key devices in almost all kinds of information storage applications, such as active images, great capacity of data stream, etc.<sup>[1]</sup>.

For increasing the storage density, the distance of tracking pitch and mark length should be shortened. In the region of far field optical recording, the diameter of focused spot is proportional to  $\lambda/NA$ :

$$d \propto \lambda/NA$$

where  $\lambda$  is writing and reading laser wavelength, and NA is optical numerical aperture of focusing lens. Therefore, the practical approach to minimize the mark length is to decrease  $\lambda$  and increase NA. The operating bands of now used CD and DVD series are 770—830 nm (near-IR laser diode) and 630—650 nm (red laser diode) respectively. Currently, the most important task is to develop blue-green-light (400—520 nm) recording media and devices for the development of high-density optical storage technology with the industrialization of blue and green laser diodes. Table 1 shows the road map of optical disk technology development. The optical disk products are moved from CD-series to DVD-series at the present time, and more research efforts are concentrated on HD-DVD and SHD-DVD disks for the next

Table 1 Road map of optical disk technology development

Time	Type	Recording wavelength (nm)	Φ5" single layer capacity (GB)	Storage density (Bg/in <sup>2</sup> )	Pitch distance (μm)	Minimum mark length (μm)	Scanning speed (m/s)	Access time (ms)	Data transfer rate (Mb/s)
Present	CD series	780	0.6	0.25	1.6	0.83	1.2~1.4	100	4.36
	DVD series	635/650	4.7	2.0	0.74~0.59	0.44~0.28	3.84	30	26~27
~2005	HD-DVD series	430~500	20~30	10~20	<0.3	<0.2	10~20	10~20	50~100
~2010	SHD-DVD series	200~350	250	100	<0.1	0.05~0.1	30	2~5	500~1000

CD: compact disk; DVD: digital versatile disk; HD-DVD: high density DVD; SHD-DVD: super-high density DVD.

century.

The new storage media are still the bottleneck in high-density optical storage. Until now, some works have been reported on phase-change, magneto-optical and photochromic materials using blue-green laser recording. The main disadvantages for inorganic materials are low CNR and erasure rate, while low transfer rate and stability for organic materials<sup>[2,3]</sup>.

Be charged with the key program of National Natural Science Foundation of China "high-density optical storage materials using blue-green laser recording", the chemical composition, microstructure, storage performance and related mechanisms of some kinds of novel high density optical disk materials have been studied in our laboratory. Some kinds of valuable inorganic and organic optical storage materials have been developed for the next generation optical disk (HD-DVD). In this paper, the progress of this program is presented and the research method and clew for super high-density optical storage materials and technologies are highlighted as well.

## 1 Short-wavelength Inorganic Optical Storage Materials

Inorganic materials possess particular advantages in rewritable optical storage. The present research includes phase-change and electron-trapping materials.

### 1.1 Ag-In-Sb-Te and Ge-Sb-Te phase-change materials

The effect of sputtering parameters (such as sputtering pressure and power) on the optical properties and short-wavelength static recording performance of AgInSbTe phase-change thin films were studied and then the optimum technical parameters were obtained. The dependence of optical constants on the film thickness of AgInSbTe phase-change thin films was also investigated and explained. The thermal-induced phase transformation properties and short-wavelength static recording and erasing performance of AgInSbTe phase-change thin films with different composition were studied and then the optimum erasing power was obtained<sup>[4]</sup>.

The effect of sputtering pressure, sputtering power and annealing temperature on the optical constants of GeTe, Sb<sub>2</sub>Te<sub>3</sub> and Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> phase-change thin films was studied. These results are significant for improving the recording and erasing performance of this kind of

thin films.

### 1.2 Oxygen-doped phase-change material and oxide material

We studied the spectral and optical properties of Ag-In-Te-Sb-O thin films before and after annealing under different sputtering conditions. This material shows different crystallization characteristics with undoped Ag-In-Te-Sb thin films from the XRD and XPS results. The reflectivity contrast of more than 20% can be obtained for this kind of thin film when irradiated by argon ion laser (514.5nm) with the recording power of 10mW and laser pulsewidth of 100ns. High reflectivity contrast can be maintained after several writing/erasing cycles<sup>[5]</sup>.

Microstructure of sublimated TeO<sub>x</sub> thin films were characterized by XPS, XRD and AFM. High reflectivity contrast can be obtained when irradiated by argon ion laser (514.5nm) with the recording power of 1.5mW and laser pulsewidth of 50ns<sup>[6]</sup>.

### 1.3 Electron-trapping materials

Many kinds of electron-trapping materials and thin films are produced, such as Eu, Sm or Ce, Sm co-doped SrS or CaS<sup>[7]</sup>. Multilayer volumetric storage based on electron trapping materials has been proposed. They also show inestimable potential for use in optical information processing fields because of their many attractive characteristics, such as high write/erase speeds (less than 5ns), limitless erasability, multilevel digital recording, capable of 3-dimensional storage, high SNR, realizing optical storage and information processing at the same time.

## 2 Short-wavelength Organic Optical Storage Materials

The organic optical storage materials possess some advantages, such as high recording sensitivity (small heat conductivity, high SNR, low melting temperature and molecule scale resolution), easy fabrication of thin films and large variety of structure and properties adjustment. Our emphases on this kind of materials include push-pull azo dye, subphthalocyanine compound, metal-TCNQ complex and so on. The preparation technique, optical properties and recording performance of them were studied in detail.

### 2.1 Push-pull azo dyes

The novel push-pull azo dyes in our study include DMA-azo, DEA-azo and DEA-diazo. The dye in polymer films were prepared with spin-coating method. An immediate large weight loss of these azo dyes in the TG analysis takes place in a narrow temperature range and the DSC analysis shows a rapid exothermic conversion with a threshold. These properties are helpful to improve signal modulation. The reflectivity contrast of more than 25% can be obtained for this kind of thin film when irradiated by argon ion laser (514.5nm) with the recording power of less than 17.5mW and laser pulsewidth of 500ns. Its optical storage performance can be further improved by adjusting its molecular structures (e.g. heterocycle structures).

## 2.2 Subphthalocyanine compounds

The three kinds of novel subphthalocyanine (Sub-Pc) dyes in our studies include bromine tri-nitro (BTN), tri-neopentoxy (BTNP) and tri-isopropoxy (BTIP) substituted subphthalocyanines. We studied their spectral and optical properties in different media (such as in solution, polymer and thin solid film) and under different solution and heat treatment conditions. We explained these results by the energy level model, aggregation properties and cone-shaped structure of subphthalocyanine dyes.

The static optical recording properties of BTN-SubPc thin films were studied using a self-developed short-wavelength optical disk tester with high NA (NA=0.85) objective lens. High reflectivity contrast (>30%) was obtained at low writing power (8mW) and short writing pulsewidth (200ns) using the Ar<sup>+</sup> laser (514.5nm) irradiation. These results demonstrate that subphthalocyanine is not only qualified for red-light recording but also a promising candidate for the recording medium of a green-light DVD-R. The leading edge, just like the falling edge, of the dye's absorption band can also be used to realize optical disk storage if an appropriate reflector were used. It provides a new clew for double-wavelength writing/reading and choosing short-wavelength recording materials<sup>[8]</sup>.

## 2.3 Metal-TCNQ complex

Ag-TCNQ and Cu-TCNQ thin films were prepared by vacuum evaporation. TCNQ molecule was modified to enhance its solubility in organic solutions and thin films with metal-TCNQ salts can be prepared by spin-coating method in near future. The optical and di-

electric constants of some kinds of metal-TCNQ thin films were determined. The proportion and temperature dependence of absorption spectral of Ag-TCNQ and Cu-TCNQ thin films were studied and investigated. Short-wavelength (514.5 nm) optical recording and erasing were realized using Ag-TCNQ and Cu-TCNQ thin films and the writing power intensity threshold of these films were measured. These results are helpful for understanding the switching mechanism of this kind of photochromic films and improving their recording/erasing properties.

## 3 Short-wavelength High-density Optical Storage Technology

We proposed a solution to the problem of the short focal depth of high-density DVD (HD-DVD) through studying super-resolution technique and short wavelength high-density optical data storage. Theoretical and experimental results indicate that the proposed method is advisable. The research includes the following aspects. (1) Proposed a new approach to super-resolution, which is through moving the low frequency light to high frequency belt but not improve the cut off frequency. This method has some advantage over the pure phase apodizers that are often used to improve the resolution of optical systems. (2) Proposed to improve the radial resolution by reducing the axial resolution according to the information capacity theory, and as a result, we can gain super-resolution in the radial direction and higher focal depth in the axial direction (from 0.6  $\mu\text{m}$  to 1.8  $\mu\text{m}$  for HD-DVD). (3) Made the axial intensity of an optical system almost equal for a wide range near the focal point through optimizing the proposed apodizer. The fold with the increased focal depth is about the same as the fold that the Strehl ratio is reduced. (4) Made the pure phase apodizer and tested the radial and axial intensity distribution of an optical system with and without the apodizer. The experimental results agree well with theoretical prediction (FWH of less than 250 nm for 514.5 nm in experiments<sup>[9]</sup>). (5) Proposed to test the point spread function of an optical system with CCD mounted onto a PZT tube through studying the point spread function test methods. (6) Studied the spherical aberration introduced by the disk cover layer thickness variation and the coma aberration caused by the disk tilt. Calculated the acceptable cover layer thickness variation and disk tilt. (7) Studied the characteristic of

the static recording system and proposed ways to minimize the recorded marks. (8) Observed marks recorded with super-resolution apodizer by SIL microscopy and AFM<sup>[10]</sup>.

#### 4 Development of Super High-density Optical Disk Materials and Technology

With the development of blue-green laser diode technology, especially the commercialization of GaN blue-ray laser diode, optical disk with minimum mark size of less than 200 nm and total volume of more than 25 GB in one side, which is called HD-DVD, become feasible with high numerical aperture and super-resolution technology. The new storage media are still a bottleneck in high-density optical storage. The demands for super-high density optical disk material include (1) appropriate optical parameters (i.e. absorption, reflectivity and refractive index) for blue-green laser recording, (2) reading, recording and erasing by single wavelength, (3) compatible with super-resolution recording and readout, readout times of more than  $10^5$ , recording/erasing cycles of more than  $10^3$ , (4) recording/erasing time of less than 200ns and preserving time of more than 10 years, etc. Until now, studies on some novel organic, inorganic phase-change materials, magneto-optical materials and photochromic materials for short-wavelength recording are under way. Doped MnBiAl<sup>[11]</sup>, magneto-optical thin film and tetra-neopentoxo phthalocyanine zinc (TNPPcZn) phase-change thin film<sup>[12]</sup> exhibit potential applications for high density optical storage.

We have reported the photothermal reversible phase change and rewritable performances of LB multilayer films of metal-phthalocyanine. The reversible change of aggregation degree of molecules will arise the reversible change of optical properties (such as absorption and refractive index) of thin films and can be used in molecular memory. Recent experimental results have shown that similar phenomena can also be observed in spin-coated<sup>[13]</sup> and evaporated phthalocyanine films.

Nanometer-scale information storage can be realized using the field (optical field or electric field) induced switching effect of some metallorganic or organic charge-transfer complexes. Photo-induced charge transfer process is an ultra-fast process and organometallic complexes are more stable than traditional organic dyes. Super high density optical storage could be realized us-

ing this kind of compound if appropriate donor and acceptor were chosen and high quality microcrystalline or amorphous thin films were prepared.

Super-resolution near-field structure technology is a new method to realize super-high density optical storage. Mark size of less than 200nm and CNR of more than 30 dB can be obtained using this technology with mask layer of Sb or AgO<sub>x</sub>.

In recent years, organic photopolymer-based high-density holographic memory, such as holographic optical disk, attracted considerable attentions. Its main advantages for practical applications are easy to be fabricated, low cost, and large variety of properties adjustment. Currently, the most important task is to realize high-performance high stability and super-high density blue-green light optical holographic storage in by optimization of materials and optical systems.

The high-density blue-green light optical disk will be one of the most powerful information carrier at the beginning of the 21<sup>st</sup> century. A huge market will be formed in this field. Our work on blue-green light optical disk material and technology will be very helpful to the development of optical storage science and information industry of our country.

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sibility for the expression regulation of different genes which could be monitored in situ when marked with *gfp* and *bfp*. With the technique of fluorescent resonance of energy transfer (FRET), the subcellular localization of different proteins in the interaction between rhizobia and host plants could also be detected.

## 5 Conclusion

A set of vectors and methods based on *gfp* genes to study the molecular genetics during the early nodulation process of rhizobia-legume symbiosis were established in this work. By using the strict promoter probe vector based on *gfpmut3*, some constitutive promoter fragments and a inducible promoter from *M.huakuii* were obtained. All the results provided strains for further study on molecular biology of *M.huakuii* and offered a new method to study gene expression regulation in the symbiosis between rhizobia and legume plants.

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