Novel phthalocyanine thin film for compact disc recordable

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In this paper, the spin-coated thin films of phthalocyanine dye are presented. Absorption spectrum of the thin film shows a comparatively broad absorption in the wavelength range 630 – 770 nm. Optical parameters of the thin film were measured by a spectroscopic ellipsometer system. 5-in CD-R discs made of this dye exhibit good performance with Yamaha 20-speed recorder. Jitters of land and pit are less than 30 ns, and the 3T–11T's signals show very good quality. This dye is a promising recording medium for CD-R with much higher recording speed.

OCIS codes: 160.4890, 210.4810, 210.4590.

The compact disc recordable (CD-R) which uses organic dye as recording layer was developed by Taiyo Yuden Co. Ltd. in 1989[1]. Due to its cheapness, good performance and whole compatibility with audio CD and CD-ROM, CD-R has become the most popular recordable optical medium today, and the annual sales in 2001 were over 1 billion units.

With the demand of high data transfer rate in computer's data reading and storage, the data transfer rate for CD-ROM has been greatly improved by increasing the speed of rotation. Now the max rotation speed of CD-ROM drives exceed 48×. CD-R also allows high speed read-back in CD-ROM drives, and further CD-R requires much higher recording speed. Today's improved CD-R discs can be recorded at speed from 1× to 16×. This is because the margin for recording speed has been widen by improving the thermal recording process through medium design[2].

Organic dyes commonly used for write-once optical media are cyanine dyes, azo dyes and phthalocyanine dyes etc. Phthalocyanine dyes show exceptional durability to reading laser beam, stability under different environments and wide writing speeds range[3]. The molecular structure of phthalocyanine compounds is shown in Fig. 1, in which M is metallic ion and R is the substitute derivative.

In this paper, we demonstrate the applicability of a phthalocyanine dye as a high speed optical recording material. Thin film of this dye was prepared by spin-coating technology. The absorption spectrum and the optical constants of the thin film were obtained. The high speed writing characteristics of 5-in disc with sandwich structure are reported and analyzed.

The samples for spectroscopic measurement were prepared by spin-coating technique. Phthalocyanine (MPc) was dissolved in dibutyl ether (DBE). After the dissolution completed, the solution was filtered with 0.5 and 0.22 μm Millipore filters. The MPc thin film was made by spin-coating on leveled glass substrate and silicon wafer with diameter of 30 mm and thickness of 1.2 mm. The film on glass substrate was for absorption spectrum measurement, and the film on silicon wafer was to obtain optical constants by a spectroscopic ellipsometer. The spin-coating process was carried out at temperature 20 °C and relative humidity 35 – 45%. The 5-in discs made of this dye were automatically fabricated on the M2 CD-R production line. The substrate was pregrooved polycarbonate disc (diameter 120 mm). The recording layer of MPc thin film was sandwiched between the substrate and a reflective layer of Ag with protective coating.

The absorption spectra of the thin film were measured on Perkin-Elmer Lambda 9 UV/VIS/NIR spectrophotometer with normal incidence of light on samples at room temperature. The complex refractive index was measured in air with a spectroscopic ellipsometer. The fabricated CD-R discs were recorded in Yamaha 20 speed CD-R writer. Recording characteristics were measured with a spindle-tester (CDCAT).

The absorption spectrum of MPc thin film is shown in Fig. 2. It has two main absorption bands at 722 and

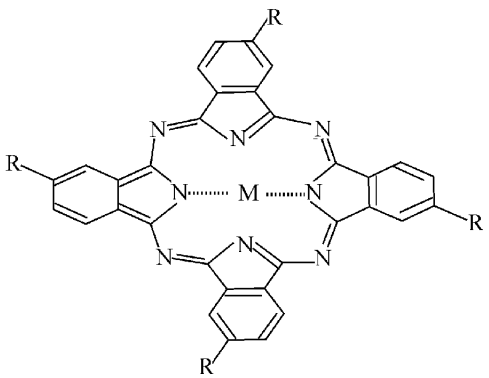

Fig. 1. Molecular structure of phthalocyanine compounds. M: substitute metallic ion; R: substitute derivative.

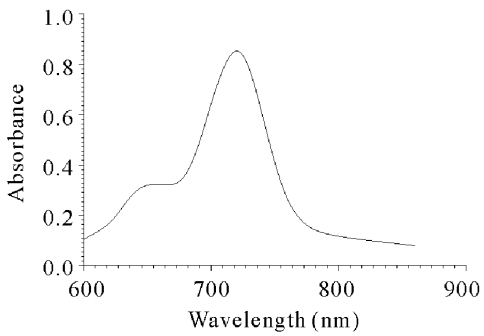

Fig. 2. Absorption spectrum of MPc film.

654 nm, which can be ascribed to the monomer and dimmer respectively[4]. The first band is much higher than the later.

The optical properties of thin films are very important for their application in optical disc. The measurement of complex refractive index (including real part n and imaginary part k) of MPc thin film was performed on spectroscopic ellipsometer. Figure 3 shows the complex refractive index of MPc thin film in the visible wavelength region. The curve of imaginary part of complex refractive index k is similar to its absorption spectrum with its highest value 1.23 at 722 nm and 0.023 at 780 nm. The strongest peak of n is located at 750 nm with its highest value 2.62, and at the optical recording wavelength 780 nm, the n value of MPc thin film is 2.18. A layer design to achieve optimum MPc thin film thickness and thus to get enough reflectivity was performed using matrix techniques. The complex refractive indices ($n - ik$, n is the real part and k the imaginary part) of each layer material given in Table 1 were used for calculation. The calculation neglects the groove, so it corresponds to mirror reflectivity. The CD-R reflectivity for different dye layer thicknesses was obtained. As shown in Fig. 4, the reflectivity of the disc oscillates and decreases as the thickness of the dye layer increases. This due to the interference between the light reflected from the polycarbonate/dye surface and that from the dye/Ag surface, and the absorbance of recording layer. We chose 150 nm as the optimum MPc thin film thickness for the CD-R fabrication. The reflectivity of CD-R blank disc at different ATIP (absolute time in pregroove) is higher than 70%, as shown in Fig. 5.

The recording mechanism of CD-R disc is a heat-mode storage, in which the thermal energy of laser light is used in the recording process and information stored as a physical change of the storage media. E. Hamada reported that both the decomposition of dye in the light absorbing layer during recording and the deformation of the substrate surface are the key factors causing the large modulation of the CD-R[5,6].

The fabricated CD-R discs of the MPc were recorded with Yamaha 20 speed CD-R writer. Then the recorded 3T−11T signals in the recording layer, T being the length of one clock cycle, were obtained by CDCAT. Land is the area between the pits in tangential direction. Effective length deviation is the length error of a specific (3T−11T) pit or land compared to its normal value, and jitter is defined as the 1σ value of the time variations between leading and trailing edges of a specific (3T−11T) pit or land as measured by Time Interval Analysis. The length deviation average of 3T−11T's lands and pits are shown in Table 2. The max length deviation is 41 ns at 10T's land and the minimal length deviation is 0 ns at 3T's land. However, all the length deviation average of 3T−11T's lands and pits are within the definition of CD-R orange book 3.1 version specification which is given in the last line in Table 2[7]. Table 3 shows the recorded signal average jitters which are less than 30 ns. Figures 6 and 7 are land-histogram and pit-histogram of 3T−11T signals respectively and show 3T−11T's signals are separated completely. This means low error rate and good quality signals can be achieved. As shown in Fig. 7, the shortest pits (3T) in this phthalocyanine CD-R were

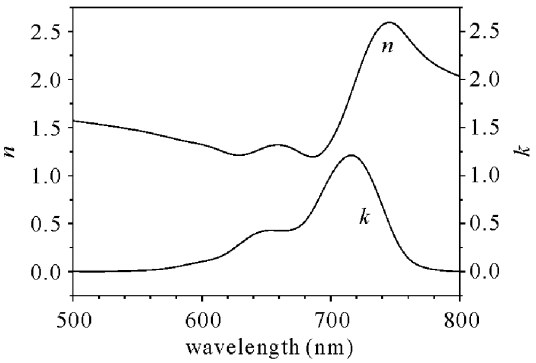

Fig. 3. Optical constants of a MPc film.

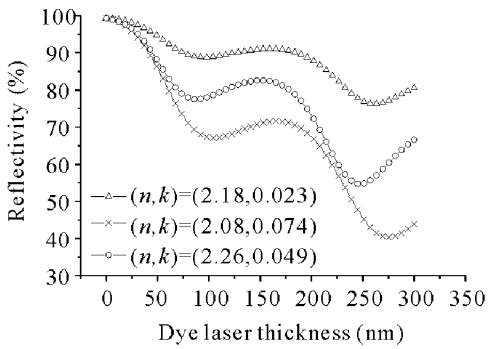

Fig. 4. Dye layer thickness dependence of disc reflectivity.

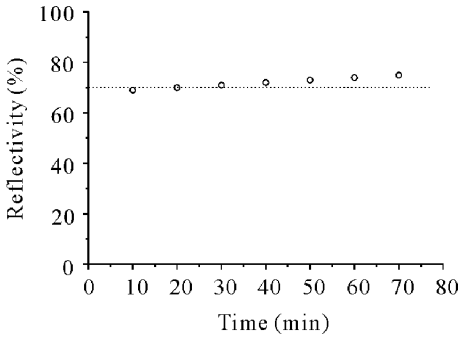

Fig. 5. The reflectivity of the fabricated CD-R disc.

Table 1. The Physical Parameters Used in Dye Layer Design

Material	Polycarbonate Substrate	Dye	Ag	Overcoat
Refractive Index	1.57	$2.18 - i0.023$	$0.03 - i5.381$	1.5
Thickness (μm)	1200		0.08	5.0

Table 2. Length Deviation Average (ns)

	3T	4T	5T	6T	7T	8T	9T	10T	11T
Land	0	−8	9	18	29	37	39	41	38
Pit	−16	−18	−11	−12	−16	−8	−3	−6	−14
Permitted	+/− 40	+/− 42.5	+/− 45	+/− 47.5	+/− 50	+/− 52.5	+/− 55	+/− 57.5	+/− 60

Table 3. Jitter Average (ns)

	3T	4T	5T	6T	7T	8T	9T	10T	11T
Land	24	24	23	24	26	26	26	26	30
Pit	30	27	24	22	21	23	24	24	25

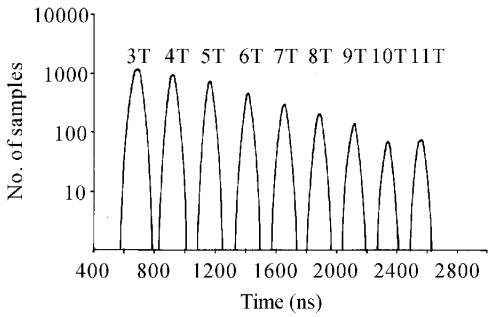

Fig. 6. Land-histogram of 3T−11T marks.

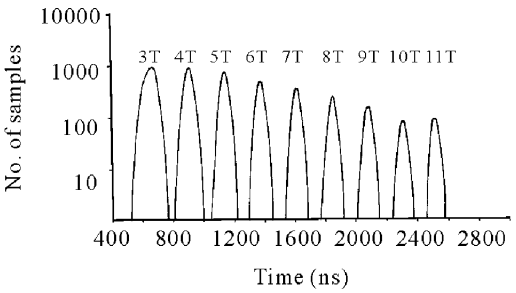

Fig. 7. Pit-histogram of 3T−11T marks.

sufficiently formed in 20 speed recording. On the other hand, it is difficult for cyanine CD-R to form the short pit sufficiently by irradiation of a short laser pulse corresponding to the high speed recording. This phthalocyanine CD-R has a wider recording speed range than Ciba's supergreen dye (a kind of phthalocyanine) CD-R ($1\times-12\times$). Although the phthalocyanine dye thin film has a lower value of imaginary part of complex refractive index k than that of some other phthalocyanine dyes, it still has good sensitivity to short laser pulse in high speed recording. The characteristic of the phthalocyanine CD-R for much higher speed recording is undergoing test in details.

In conclusion, the thin film of MPc dye has a sharp absorption band near 750 nm and very small absorbance at wavelength 780 nm. The reflectivity of the phthalocyanine CD-R is over 70%, and exhibit good performance in Yamaha 20 speed writer. These results show the MPc thin film is promising high speed recording media for CD-R.

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