Jpn. J. Appl. Phys. Vol. 42 (2003) pp. 997–999
Part 1, No. 2B, February 2003

Thermal and Optical Properties of Organic Dyes for Super-Resolution Recordable Disks

Hao-Hsien CHIANG[1], Wei-Chih HSU[1,2], Song-Yeu TSAI[1], Mei-Rurng TSENG[1], Shih-Peng HSU[1], Tien-Tsan HUNG[1], Chin-Jung CHANG[1] and P. C. KUO[2]

[1]*Materials Research Laboratories, Industrial Technology Research Institute, Bldg. 77, 195-5 Chung Hsing Rd., Section 4 Chutung, Hsinchu, Taiwan 31015, R.O.C.*
[2]*Institute of Material Science and Engineering, National Taiwan University, No. 1, Roosevelt Rd., Sec. 4, Taipei 106, Taiwan, R.O.C.*

(Received August 14, 2002; revised manuscript received October 18, 2002; accepted for publication October 28, 2002)

We have studied the characteristics of super resolution optical disks with an organic dye used for the recording layer. It was demonstrated that cyanine dyes with either high decomposition temperature or low absorption show good readout durability and high carrier-to-noise ratio (CNR). [DOI: 10.1143/JJAP.42.997]

KEYWORDS: super-resolution disk, organic dye, decomposition temperature, absorption, carrier-to-noise ratio (CNR)

1. Introduction

For optical data storage disk, the theoretical limitation of diffraction is about 0.6λ/NA where λ is the recording/reading laser light wavelength and NA is the numerical aperture. The super-resolution technique[1–8)] using a below-diffraction-limit aperture within the readout spot is an effective method of improving recording density which involves simply inserting a mask layer on a disk without changing the laser diode or optical device. Previously, we reported on the first super-resolution disc with an organic dye recording layer, and the results showed that a mark size below 150 nm, which is beyond the limit of diffraction, could be read out at reading power of 3 mW; the carrier-to-noise ratio (CNR) was 12 dB.[8)] In this paper, the CNR of the 150 nm mark size is 18.5 dB at a reading power of 3 mW. The thermal stability of the recording marks for the super-resolution recordable disk is poor when the disk is read out at a high reading power. Therefore, selecting stable materials for the recording layer is one way of solving this problem. The recording layer made of organic dye with high decomposition temperature possess essuitable thermal stability during continuous readout.

2. Disk Structure and Experimental Conditions

We designed the super-resolution disk structure presented in Fig. 1. The layers are PC(polycarbonate substrate)/SiN_x/Sb/SiN_x/dye/Au. The films other than the recording layer were deposited on a polycarbonate substrate by RF magnetron sputtering at the background pressure of less than 5×10^{-6} Torr and argon pressure of 3 mTorr. The substrate was a conventional pregrooved polycarbonate disk, 0.6 mm thick and with 0.74 μm track pitch. We used an antimony, mask layer and SiN_x protective layers. An organic dye was used for the recording film, which was deposited by spin coating on the sandwich layers of SiN_x/Sb/SiN_x. The optical density (OD) of dye was controlled carefully. Gold was sputtered for the reflective layer. Finally, an UV-curing resin was coated for protection. Thermogravimetric analysis (TGA) was carried out at a heating rate of 10°C/min in a N_2 atmosphere. Recording and readout were performed using a digital versatile disc (DVD) test system (DDU-1000, Pulstec Co.) with wavelength of 635 nm and NA of 0.6. The recording mark size was controlled carefully by adjusting the recording power, pulse duration and linear velocity in consideration of thermal diffusion of the recording mark in the organic layer.

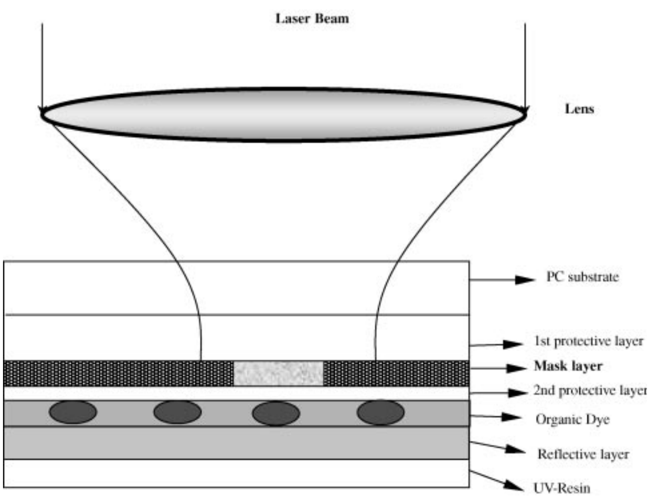
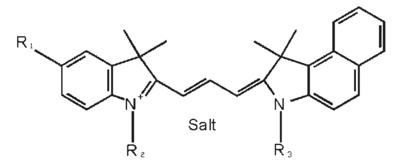


Fig. 1. Disk structure.

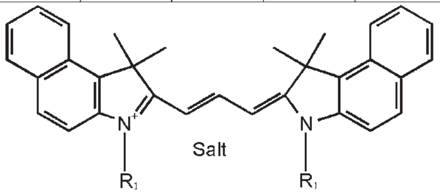
3. Results and Discussion

In the layer structure of a Sb-type Super-RENS disc, an optical near field is generated at a transparent aperture within the Sb mask layer and it interacts with the recording marks. Therefore, the interface layer between mask and recording layers should be thin enough (<50 nm), within a near-field region, to detecting signal of below-diffraction-limit mark length (<265 nm) using a laser beam of 635 nm wavelength. Tsai and Lin[9)] and Liu *et al.*[10)] propose that the SiN_x/Sb/SiN_x sandwich layer not only works a ‘‘aperture’’ for reducing spot size but also has other enhancement effects of optical intensity. Physically the phenomena are ‘‘surface plasmon resonance’’ (SPR) effects. The enhanced near field interacts with the recorded mark on the organic dye layer and is scattered into the far field. Therefore below-diffraction-limit mark length could be read out. Since the super-resolution phenomenon occurs at high readout power, the organic dye materials and mask layer should have high thermal stability.

Four cyanine dyes were synthesized for analysis as to their use as a recording media. The molecular structures of the dye are shown in Fig. 2. Dyes B and C have absorption peaks at around 573 nm (in TFP solution), dye D, at around 587 nm (in TFP solution) and dye A, at around 568 nm (in TFP solution). The absorption spectrum of dye A in thin film



Name	Salt	R1	R2	R3	λ max	TGA
Dye A	PF_6	Cl	Me	Me	568	260
Dye B	PF_6	Cl	n-Bu	n-Bu	573	275
Dye C	PF_6	Me	n-Bu	n-Bu	573	263



Name	Salt	R1	R2	R3	λ max	TGA
Dye D	ClO_4	n-Bu	---	---	587	245

Fig. 2. The molecular structures of dyes.

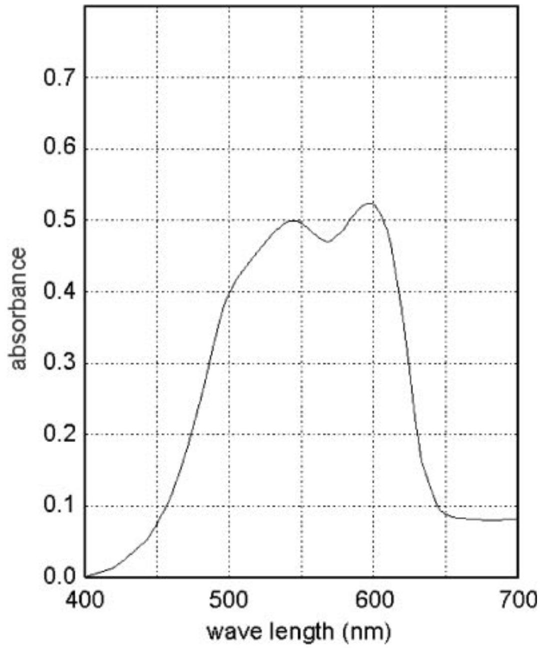


Fig. 3. Absorption spectrum of dye A thin film.

is shown in Fig. 3. It has sharp and strong absorption bands. The dye has two absorption bands, and the second absorption band (on the long wavelength side) at around 600 nm is more influential. The absorption weakens rapidly at around 635 nm, which is the wavelength for recording and readout in DVD-R. Dye B has a high decomposition temperature ($T_d = 275°C$, as determined by TGA) and dyes A and C have lower T_d (about 260°C). T_d of dye D is the lowest at 245°C. Figure 3 shows the TG chart of dye B. TGA revealed a large weight loss of the dye in a narrow temperature range. The weight reduction relative to the temperature in the main weight reduction process is about 2%/°C. By TGA of the dye, the total weight reduction in the main weight reduction process was found to be 67%. The thermal property of a dye strongly affects the fabrication of a small and sharp recording mark edge. Using a dye, whose thermal decomposition occurs over a wide temperature range will result in undesirable excess deformation. The thermal conductivity of the dye layer causes thermal interference between two adjacent recording marks and this causes spatial limitation of high recording density. A sharp threshold of dye decomposition, as indicated by the steep and large weight reduction in Fig. 4, is desirable.[11)]

Figure 5 shows the CNR dependence on the mark size for recordable disks with mask layers of different dyes for comparison with conventional disks without the mask layer. The optimal readout power for the conventional disks was

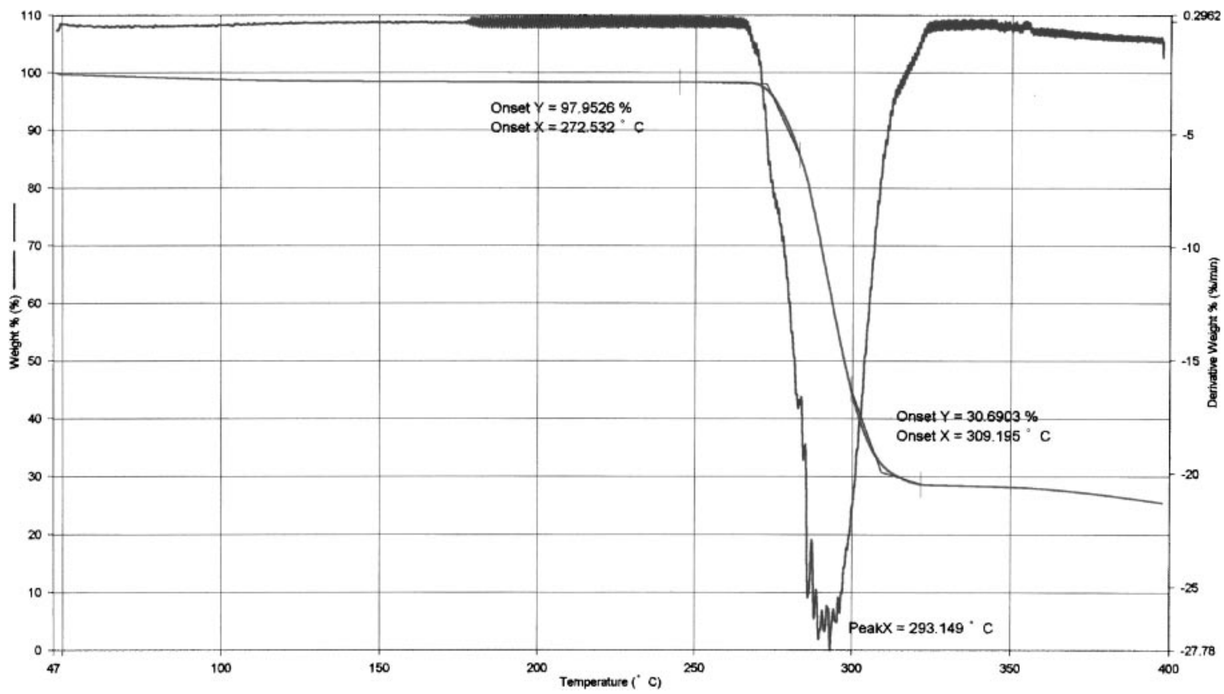


Fig. 4. TG chart of dye B.

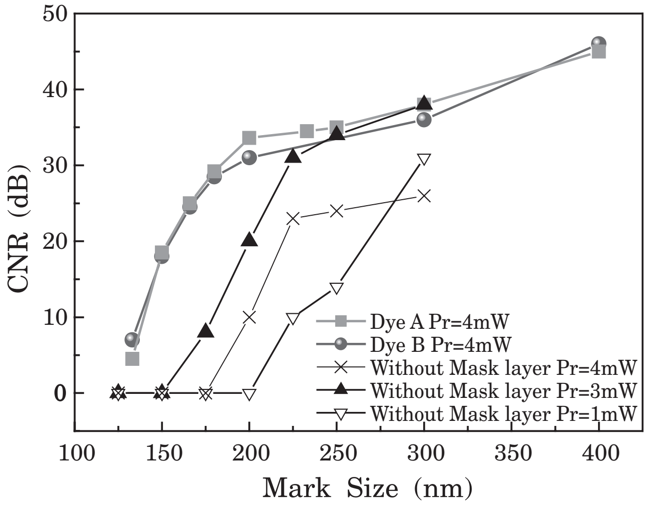


Fig. 5. CNR and mark size characteristics of sample disks with dye A and dye B for recording layer.

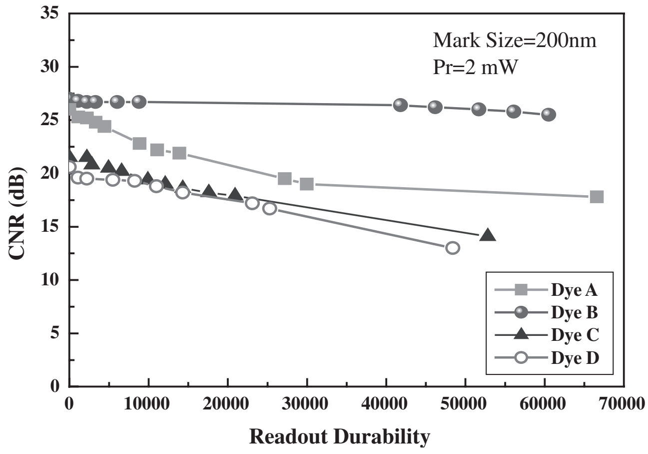


Fig. 6. The readout durability of sample disks with dye A, dye B, dye C and dye D for recording layer.

3 mW. The CNR of the conventional disks rapidly decreased when the mark lengths decreased, and the signals were no longer detected at mark lengths of less than 150 nm at a reading power of 3 mW. In contrast, the super-resolution disks possess CNR of 18.5 dB of the 150 nm mark size at $P_r = 4$ mW. The CNR of the 130 nm mark size can be read out at a reading power of 4 mW. Theoretically, the mark resolution limit is defined as half the diffraction limit (λ/4NA ~265 nm). Mark sizes as small as 130 nm and 150 nm can be read out by using super-resolution technique. The reason why it is possible to read out recorded marks with lengths below the cut-off (265 nm) on the conventional disk at high read out power may be that as the reading power of the focused spot is increased to a high power, a near field is generated around each small mark. When the distance between marks is reduced to within a near field coupling distance. The near fields interact with each other and scatter into a far field. Then the dynamic tester could detect the signals of marks below the diffraction limit. Similar experimental results and conjecture were proposed in previous reports on the super-read-only-memory (ROM) disc and without-mask-layer $Ge_2Sb_2Te_5$ film.[12,13] However, further studies and evidence are necessary.

The readout durability for 200-nm-mark trains at $P_r = 2$ mW and CLV = 3.5 m/s of the super-resolution disk is shown in Fig. 6. The CNR of dye A is 25.5 dB, dye B 27 dB, dye C 22 dB, and dye D 20 dB. The readout durability of the CNR of dye B shows almost no change after 6×10^4 cycles. As a result, it is concluded that dye B with high T_d ($T_d = 275$°C) and moderate absorption has better thermal stability than dye C or dye D with low T_d and high absorption.[14]

4. Conclusion

We have investigated the super-resolution properties of recordable disks. A mark size below 150 nm, which is beyond the limitation of diffraction, can be read out at a reading power of 4 mW. The readout durability is more than 6×10^4 cycles for the high T_d and moderate-absorption dye that shows good thermal stability.

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