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New Write-One Optical Media Using Near Infrared Absorbing Metal Complex Dyes with Indoaniline-Type Ligand

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NEW WRITE-ONCE OPTICAL MEDIA USING NEAR INFRARED ABSORBING METAL COMPLEX DYES WITH INDOANILINE-TYPE LIGAND

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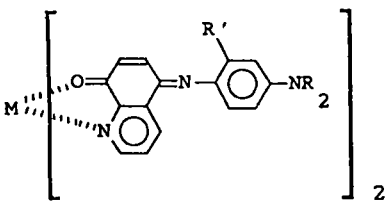
ABSTRACT New optical media have enough recording performance to be used as write once optical media: moreover these film show good light stability.

INTRODUCTION

Organic dyes which are applied to the field of diode-laser optical storage have attracted considerable attention.[1,2] As diode-lasers used in this field emit near-infrared light at 780-830nm, the optical recording media have to absorb near-infrared light efficiently. Recently, we have reported the synthesis of new metal complex dyes with N,O-bidentate indoaniline-type ligands, e.g. 1.[3,4] The compounds in formula 1 have intense absorption bands at 750-800nm in chloroform solution.

In this paper, we report the film properties and recording characteristics of such metal complex dyes with indoaniline-type ligands.



1

1a M=Ni,Z=ClO4,R'=CH3,R=C2H5
1b M=Co,Z=ClO4,R'=CH3,R=C2H5
1c M=Ni,Z=BF4, R'=CH3,R=C2H5
1d M=Ni,Z=ClO4,R'= H ,R=C2H5
1e M=Ni,Z=ClO4,R'=CH3,R=C3H7(n)
1f M=Ni,Z=ClO4,R'=CH3,R=C4H9(n)

EXPERIMENTAL

The write-once optical media comprising the dye films were fabricated by spin-coating on the injection-molded polycarbonate substrate with 1.6μm pitched pregrooves. The thickness of the dye films was measured by taly-step. Practical recording characteristics were measured by using an optical head with an objective lens of N.A.~0.50 and an 830nm diode laser. The laser diode beam was focussed down a spot diameter of ~1μm onto a dye layer through the substrate. The carrier-to-noise ratio (CNR) and second harmonic distortion (SHD) of reproduced signal were measured under the condition of the recording frequency of 1.0 MHz (duty ratio of 50%), the linear velocity of 4m/s and the reproducing laser power of 0.6mw.

RESULTS AND DISCUSSION

The recording layer was conveniently prepared by spin-coating a solution of dye 1 onto a polycarbonate substrate. The thickness of the dye films was 80nm. The spectrum absorbance in choloform solution and the optical properties of dyes 1a ~ 1f films are summarized in Table-1. Such dye films showed sufficient absorbance and reflectance at the oscillation wavelength of 780-830nm diode-lasers.

TABLE I. Optical properties and film stabilities of dyes.

Dye	Solution in $CHCl_3$		Film		
	λmax (nm)	$\varepsilon \times 10^{-5}$	λmax (nm)	Reflectance[a] (%)	Stability[b] (R500/R0,%)
1a	795	1.55	795	45	90.5
1b	802	0.68	795	43	41.5
1c	795	1.54	800	40	80.5
1d	785	1.39	792	35	72.6
1e	799	1.50	801	43	92.4
1f	801	1.57	810	41	97.0
Cyanine	-	-	800	42	97.2

a) Incident light intensity at 830nm measured by spectrophtometer.
b) R500/R0 indicates the ratio of reflectance at 500hrs and 0hr. Accelerated stress condition at 65°C, 85%RH for 500hrs.

Table-I also shows that the chemical and physical stabilities of these dye films were strongly influenced by the nature of metal(M), anion(Z), and substituent(R') of the dye molecules 1. The reflectance of dyes 1b, 1c and 1d largely changed after standing for 500hrs at 65°C , 85%RH, whereas the reflectances of dyes 1a,1e and 1f were almost unchanged. The dye 1f film indicated the best stability.

Figure-1 shows the CNR and SHD of reproduced signal of dye 1f film vs recording power. A CNR of more than 55dB and an SHD of less than -35dB were observed at the recording laser power of 6.0mw. From these experimental results, it is believed that the films using metal complex dyes have enough performance to be used as write-once optical media. The stability of the written data under continuous reading was tested with the optical recorder system. No remarkable degradation of CNR was observed even upon 10^6 times at read power of less than 0.6mw. This level is satisfactory to be used as write-once optical media.

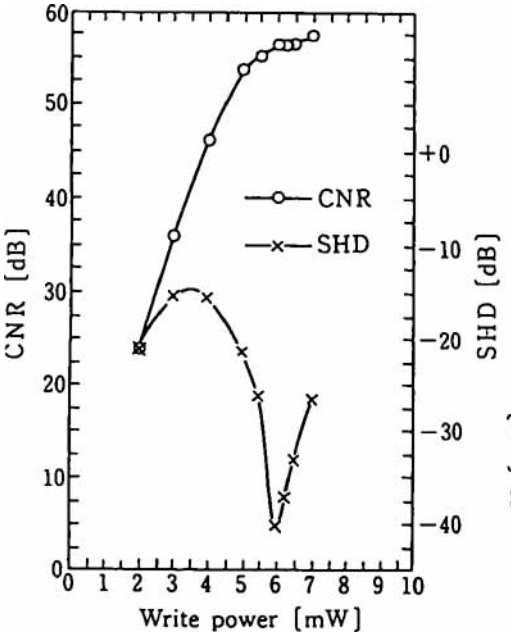


FIGURE 1. Recording characteristics of dye(1f) film

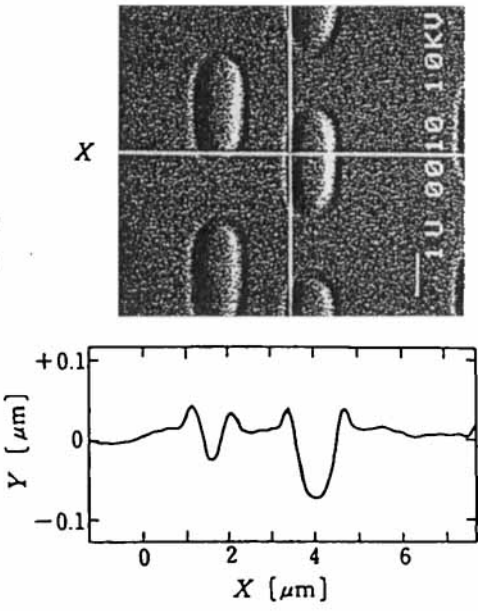


FIGURE 2. SEM micrograph and cross section of pits

Figure-2 shows a photograph by SEM and a cross section of recorded pits. As suggested by a high CNR and a low SHD, the recorded pits have smooth rims and symmetrical shapes. Furthermore, it was found that the depth of the pit was nearly equal to the thickness of the dye film, and that 50~70vol.% of the dye was sublimated by exposure to the laser beam.

Furthermore, it is notable that the medium using dye 1f film has excellent resistance to visible & UV light. The result is given in Figure-3. The reflectance of this medium was little changed after irradiation for 60hrs with Xenon Fademeter. Whereas the reflectance of cyanine dye containing Ni-dithiene quencher, which is currently used as an optical recording medium, was decayed to 20% of its original value.

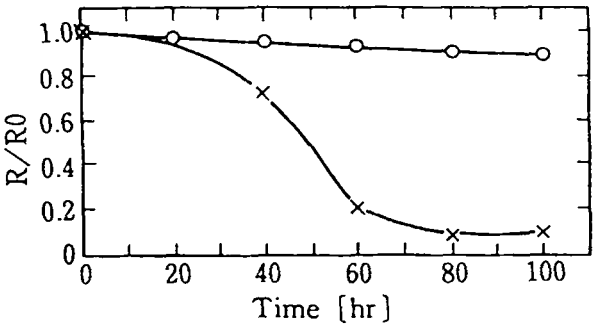


FIGURE 3. Photolytic stability
(—○— : metal complex dye 1f
—×— : cyanine dye)

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