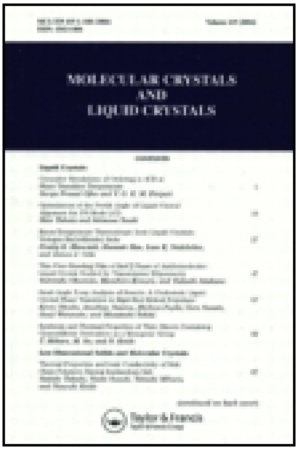

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MULTIPLE OPTICAL MEMORY USING PHOTOCHROMIC SPIROPYRAN AGGREGATES

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Abstract Multiple recording technology is particularly important for the high density optical memory. Through investigating the aggregate-forming ability of the new photochromic spiropyrans, we have developed five novel spiropyrans, the aggregates of which have sharp absorption bands at different wavelengths. We have fabricated a recording medium stacked with the five kinds of aggregate layers and confirmed ten multiple optical recording characteristics by combining the five multiple frequency recording with the recording by two mutually perpendicular linear-polarized lights.

INTRODUCTION

Optical memory is one of the high density recording media, which have been actively investigated for advanced information network. Of the various optical recording materials, photochromic compounds have high possibility as the rewritable optical memory. One of the important properties for photochromic compounds is a thermal stability. In order to improve the instability, many new photochromic compounds have been studied such as fulgide compounds[1], diarylethene derivatives[2], spiropyran's aggregates[3], etc.

Our group previously synthesized novel photochromic spiropyran SP1822 with two long alkyl chains and found that the colored state of SP1822 forms a typical J-aggregate, which shows a good thermal stability and a very sharp absorption band[4]. Utilizing these characteristics we have proposed a new rewritable multi-frequency optical memory system using many aggregated spiropyrans whose absorption bands are differnt from each other[5]. Recently we have developed some kinds of novel spiropyrans forming J- or H-aggregates[6,7,8] and have experimentally confirmed the possibility of the four multiple frequency recording using four kinds of aggregated spiropyrans[9].

In this paper, the combination of the multi-frequency recording and the recording by irradiation of linear-polarized laser lights is newly proposed, and the characteristics of ten-multiplicity is shown by using the multi-frequency rcording medium with five aggregated spiropyrans.

MULTIPLE RECORDING

The multi-frequency recording medium[5] is comprised of thin films of several aggregated spiropyrans, layered in order on a substrate, which have sharp absorption bands at different wavelengths. The multiple recording data are independently recorded in each aggregate layer on one recording spot by several laser lights corresponding to absorption bands of the each aggregate layer. Therefore, the density of recording increases by the number of spiropyrans.

By irradiation of linear-polarized light, the color of spiropyran aggregate having the transition moment parallel to the direction of light polarization, is selectively bleached. In Figure 1 the principle of polarized recording to multiple recording medium is shown. Aggregated spiropyran films have no anisotropy as a whole in plane. At an initial state, both absorption spectra of the films by a linear-polarized light and another one perpendicular to that are coincident

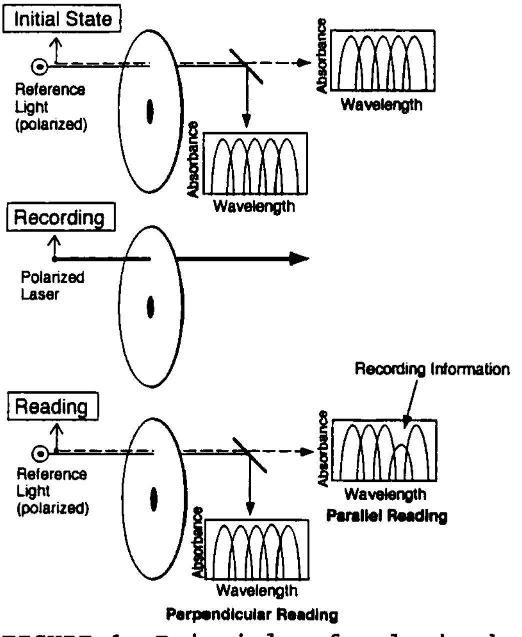


FIGURE 1 Principle of polarized recording to multiple recording medium.

with each other. When recorded by a linear-polarized laser light of a certain direction (named as polarized recording), only spiropyran aggregates of the same transition moment's direction changes selectively to decolored state. Moreover, another recording can be carried out to different aggregates of perpendicular direction in the same spiropyran layer by irradiating the other polarized light of perpendicular direction. The reading procedure is practiced by white lights consisting of two mutually perpendicular linear-polarized lights. Distinction between these two records is possible owing to the anisotropy of their absorption spectra. Thus, it is possible to double multi-frequency recording density by this polarized recording.

EXPERIMENTAL

The molecular structures of five aggregated spiropyrans, SP1822, BSP1822, MSP1822, SP150 and CSP0122, are shown in Figure 2. A multi-frequency recording medium comprised of aggregated spiropyran layers was prepared by spin coating technique on a glass substrate. Its structure is shown in Figure 3. Each spiropyran layer was comprised of the composition mixed with polyion complex(PIC[10]) and additives indicated in the figure. Between these spiropyran layers, double separation layers were formed.

Multiple recording was performed with linear-polarized visible laser lights, which was irradiated from pulsed dye laser excited by a XeCl excimer laser (pulse width 25nsec) and polarized through a polarizing prism. The changes in

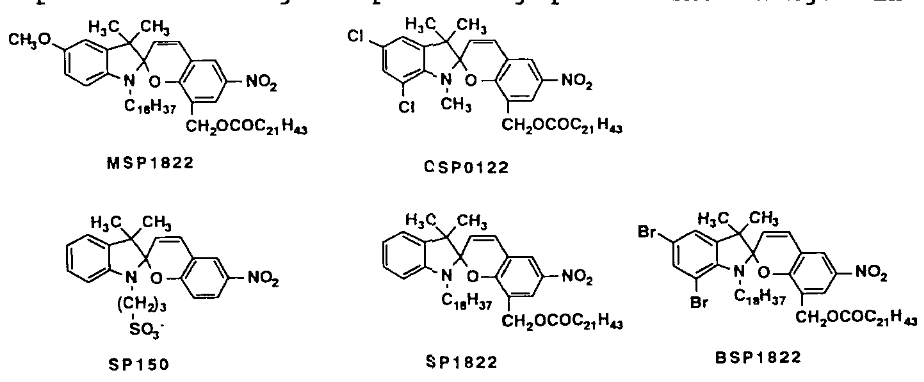
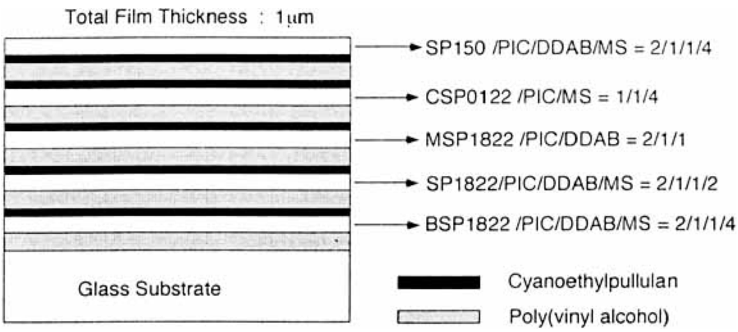


FIGURE 2 Molecular structures of spiropyrans.

absorption spectra before and after polarized laser irradiation were measured with a multichannel photodetector and a polarizing prism. Wavelengths and energies of polarized laser lights for multiple recording were 650nm,15.5mJ/cm^2 for BSP1822, 618nm,21.6mJ/cm^2 for SP1822, 485nm,25.4mJ/cm^2 for MSP1822, 530nm,22.0mJ/cm^2 for CSP0122, and 580nm,23.6mJ/cm^2 for SP150, respectively.



PIC:Dioctadecyidimethylammonium polystyrene sufonate
DDAB:Dioctadecyidimethylammonium Bromide , MS:Methyl stearate

FIGURE 3 Multi-frequency recording medium and compositions of each spiropyran's layer.

RESULTS AND DISCUSSION

The absorption spectra of five spiropyran aggregates are shown in Figure 4. Their aggregates are J-aggregate for BSP1822, SP1822, SP150, H-aggregate for CSP0122, MSP1822. Thier peak values of sharp absorption bands are 650nm, 618nm, 578nm, 531nm, 490nm, respectively. The mixture of spiropyrans, PIC and additives are the most suitable composition for aggregation of each spiropyran.

Figure 5 shows the dependence of changes in maximum absorbance at 618nm of J-aggregated SP1822 on irradiated one pulse energy of linear-polarized laser light (618nm). A_0 and A are the absorbance before and after laser irradiation, respectively. J-aggregate of SP1822 exhibits nonlinear response to the one pulse energy, that is, it has no response in the region below threshold energy of about 5 mJ/cm^2. This nonlinearity to laser irradiation relates with the disaggregation behaviour caused by the generated heat,

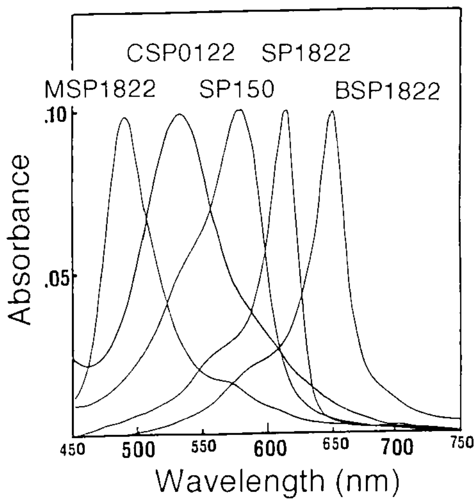


FIGURE 4 Absorption spectra of five aggregated spiropyrans.

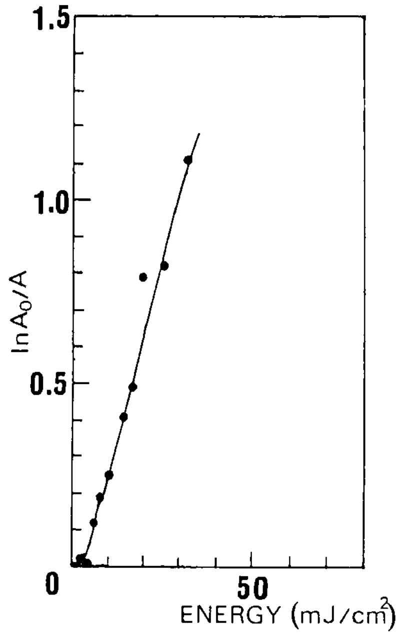


FIGURE 5 Absorbance changes of J-aggregated SP1822 by irradiation of linear-polarized one pulse laser.

and the threshold energy is smaller than that for nonpolarized laser irradiation[9]. Spiropyran aggregates in the polarizing direction of laser light selectively react and the linear-polarized recording is effectively carried out, since their transition moments are coincident with polarizing direction. Furthermore, other spiropyran aggregates exhibited the similar recording properties as SP1822. The above-mentioned multiple recording conditions were decided from results of these recording properties.

Figure 6 shows a series of spectral changes before (solid line) and after (dotted line) the irradiation of linear-polarized laser lights to multiple recording medium. The dash-dotted lines indicate difference absorption spectra of before and after recording. Left side and right side figures are the spectral changes measured by a linear-polarized reading light parallel to recording laser's polarization (parallel reading) and that by the reading light perpendicular to it (perpendicular reading), respectively. In spite of the overlap of each absorption band in Figure 4, each spectral change of parallel reading occurs almost independently in each absorption band and each one of perpendicular reading hardly occurs.

It is considered that such independency for multiple recording depends on the existance of threshold energy in nonlinear properties of aggregates. For multi-frequency recording, in overlap regions of absorption between two adjoining frequencies the sensitivity is favourably depressed owing to the threshold energy[9]. And for polarized recording, the sensitivity of aggregates perpendicular to linear-polarized laser light is very low also.

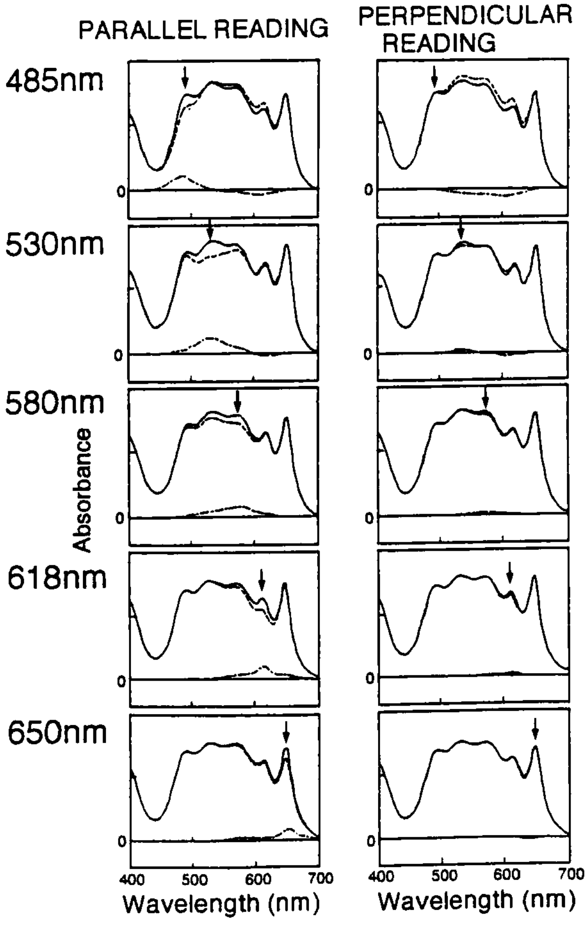


FIGURE 6 Absorption spectra of multiple recording medium before (solid line) and after (dotted line) linear-polarised laser irradiation. Dash-dotted lines indicate difference absorption spectra.

However, in recording at 485nm, the absorption of MSP1822 was decreased for parallel reading and the unnegligible spectral increase appeared at near 500-600nm for both parallel and perpendicular readings. This increased absorption is ascribed to the absorption of colored monomers due to the disaggregation of MSP1822 H-aggregate. That is, this result shows that H-aggregates having the transition moments parallel to the recording polarized light are disaggregated, the disaggregated colored monomers lose a initial orientation of aggregates and show an isotropic distribution in plane. This increase of absorbance causes a noise signal in difference spectrum region. In order to get high SN ratio, the correction of spectra for MSP1822 was performed as shown in Figure 7. That is, the absorbance of colored monomer of MSP1822 was subtracted from both spectra of parallel and perpendicular readings after recording. As the result of this correction, the increase of absorbance in both spectra was cancelled and the spectrum change of recording for H-aggregate of MSP1822 was shown only in difference spectrum of parallel reading.

Thus, it has been confirmed that, intrinsically, such disaggregation proceeds independently in each layer of spiropyran aggregates under the corresponding laser irradiation and their absorbance change can be distinguished clearly as the recording signal by the parallel and the perpendicular reading to linear-polarized recording. The

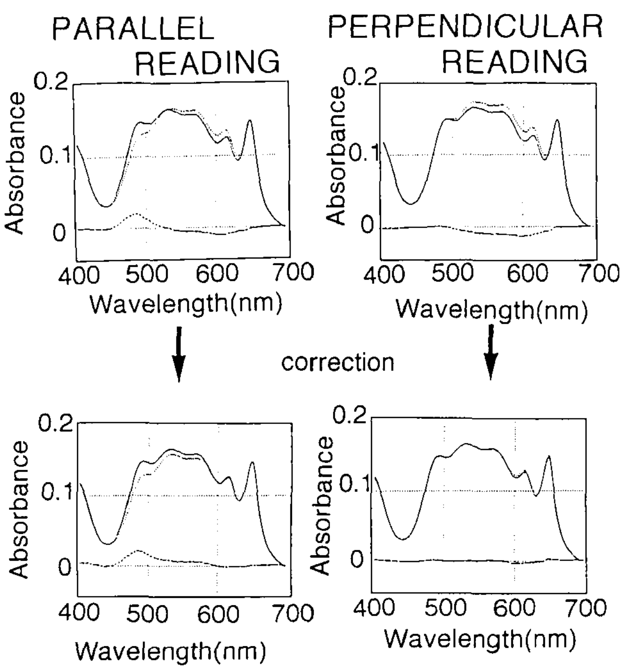


FIGURE 7 Correction of spectra by subtracting absorbance of monomer for MSP1822.

independency of both multi-frequency and polarized recordings have been obtained without signal overlap, and ten-multiple laser recording has been confirmed experimentally by the combination of five multi-frequency recording and linear-polarized light recording.

CONCLUSION

We have proposed new multiple optical memory by the combination of multi-frequency and polarized recording. Using the recording medium stacked with the five spiropyran aggregate layers, ten-multiple optical recording characteristics was confirmed experimentally. In future, such multiple recording technology would particularly become important and would be further expected as a promising method for increasing the optical recording density.

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