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Synthesis and optical properties of an azo metal chelate compound for optical recording medium

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Abstract

An azo nickel chelate compound has been synthesized. Smooth thin films have been prepared by spin-coating. The absorption, transmission and reflection spectra of the films were measured. The optical constant (complex refractive index $N = n + ik$) of the film on single-crystal silicon has been determined using scanning ellipsometer, and the complex dielectric function (ε) as well as absorption coefficient (α) were then calculated. The optical recording medium was prepared by spin-coating on a PC substrate with aluminium as reflective layer. Dynamic optical recording test of the disc showed that the carrier-to-noise (CNR) of 45dB was obtained.

Keywords: Azo dye; Azo metal chelate dye; Thin film; Optical properties; Optical recording medium

1. Introduction

Azo dyes are by far the most important class of dyes for the textile industry [1]. They are receiving increasing attention as materials for non-linear and photoelectronic applications [2], especially in optical information storage [3]. Optical recording employing a laser has developed significantly in recent years, as it makes the storage of high density information recording and its reproduction possible. In general, the recording is conducted in such a manner that on absorption of the irradiating laser beam energy, a portion of the recording layer undergoes thermal deformation such as decomposition, evaporation or dissolution. Further, the reproduction of the recording information is conducted by reading the difference in reflectance between the portion where such a deformation was formed by the laser beam and a portion where no such deformation was formed. Accordingly, the optical recording medium is required to efficiently absorb the laser beam energy. Organic dyes have been developed since 1985 as successors to inorganic Te materials for write-once optical memory discs. Organic dyes, such as cyanines and phthalocyanines have been used. Azo metal chelate compounds have also been developed in view of their excellence in sensitivity as an optical recording medium. Chelation of a metal to the azo and other groups in the azo dye results in an

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improvement of the light fastness of the metallized azo dye. Hence, problems of storage stability and weather resistance of the optical recording medium using such compounds can be resolved. Various constructions have been patented for optical recording media using dyes of this type [4–7]. However, the spectroscopic and optical properties of thin films of azo metal chelate compounds have not been reported. In this paper we describe the synthesis of an azo nickel chelate compound (Fig. 1). Results of the spectroscopic and optical characteristics, as well as optical recording behavior of the metal chelate dye thin films, show that the azo metal chelate compound is a promising candidate for use as an optical recording medium.

2. Experimental

2.1. Synthesis of the azo dye and its nickel chelate compound [8,9]

2.1.1. Diazotization

2-Amino-6-carbomethoxybenzothiazole 1.04 g (5 mmol) was dissolved in 10 ml 85% phosphoric acid. The solution was then cooled to 0–5°C in an ice-brine bath and maintained at this temperature. Sodium nitrite 0.38 g (5.5 mmol) was added as a solid, over a period of 20 min. Stirring was continued for 2 h, keeping the temperature between 0–5°C. Finally, a small amount of urea was added to destroy excess nitrous acid.

2.1.2. Coupling

N,N-Diethyl-*o*-anisidine-4-sulphonic acid 1.425 g (5.5 mmol) was dissolved in a mixture of 10 ml water and 5 ml acetic acid. The solution was cooled to 0–5°C in an ice-brine bath. The diazonium solution was added portionwise to the coupling component, and maintained at 0–5°C for 2 h. The mixture was kept overnight, while the temperature rose to ambient. After filtering, 1.44 g crude dye was obtained (yield 60.1%). The crude dye was purified by column chromatography on silica gel using 2-propanol as eluant, giving the pure product. λ_{max} (MeOH, ε): 559 nm(1.45×10^4), MALDI-TOF-MS($C_{20}H_{22}N_4O_6S_2$) m/z: 479 $(M+1)^+$, 501 $(M+Na)^+$.

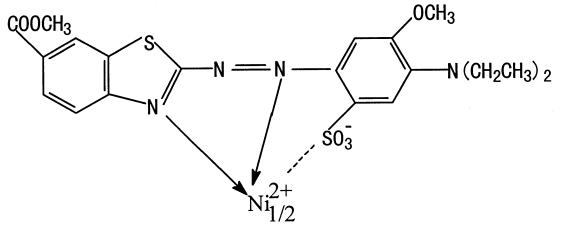

Fig. 1. Structure of the azo nickel chelate compound.

2.1.3. Metallization

The azo dye 0.245 g(0.51 mmol) was dissolved in 20 ml methanol and then 5 ml methanolic solution of nickel acetate (0.3 mmol) was added slowly. The mixture was stirred for 24 h at room temperature. The precipitate was filtered, washed with methanol, dried, giving 0.109 g of the azo nickel chelate dye (yield 41.9%), λ_{max}(chloroform, ε): 625 nm(4.65×10^4), 683 nm(5.58×10^4), MALDI-TOF-MS ($C_{40}H_{42}N_8O_{12}S_4Ni$) m/z: 1035(^{58}Ni), 1037(^{60}Ni) $(M+Na)^+$.

2.2. Sample preparation

The azo nickel chelate dye was dissolved in 2,2,3,3-tetrafluoro-l-propanol, to give a concentration of 30 mg/ml solution. The solution was filtered using a 0.22 μm micropore filter, to obtain the coating solution. Smooth films were spin-coated on clear optical glass and single-crystal silicon (diameter, 30 mm; thickness, 1.2 mm) substrates. The optical recording medium was fabricated on pregrooved polycarbonate substrate (diameter, 12 cm) by spin-coating. An aluminium reflective layer was fabricated by vacuum sublimation (2.7×10^{-3} Pa) on the dye layer. The substrates were kept at room temperature throughout the deposition process.

2.3. Instrument and methods

Mass spectra were determined on a matrix assisted laser desorption/ionization time-of-flight mass spectrometer (MALDI-TOF-MS) using a Bruker Biflex III. Absorption, transmission and reflection spectra were performed on a Perkin–Elmer Lambda 9 UV/VIS/NIR spectrometer.

Complex refractive index $N(N = n + ik)$ was determined by a scanning ellipsometer, details of which have been reported elsewhere [10]. The experimental set-up of the dynamic recording tester has also been previously reported [11].

3. Results and discussion

3.1. The optical properties of the azo nickel chelate dye films

The optical properties of the dye films can be described by the complex refractive index (N) and the complex dielectric function (ε). The ellipsometric spectra of the azo nickel chelate dye film, spin-coated on single-crystal silicon, were investigated on a scanning ellipsometer. The variation of refractive index $N(N = n + ik)$ with wavelengths (λ) was obtained. Fig. 2 gives the real part n and imaginary part k of the complex refractive index of the film with thickness of 70 nm in the visible and near-IR regions. The real part n of the complex refractive index generally relates to dispersion, while the imaginary part k provides a measure of the dissipative rate of the wave in the medium. Usually, a high n value and low k value are a good match for high reflectance. As shown in Fig. 2, the value of n is 2.26, while the value of k is 0.062 at 780 nm, corresponding to the output wavelength of the GaAs laser.

The real part ε_1 and imaginary part ε_2 of the complex dielectric function $\varepsilon(\varepsilon = \varepsilon_1 + i\varepsilon_2)$ are related to the n and k of the complex refractive index by the following two equations respectively:

$$\varepsilon_1 = n^2 - k^2, \varepsilon_2 = 2nk$$

From the values of n and k, the values of ε_1 and ε_2 can be calculated, and are shown in Fig. 3.

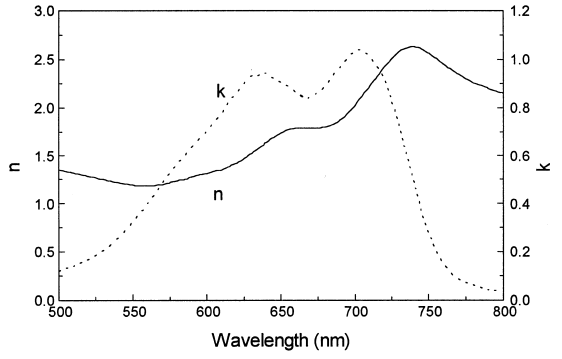

Fig. 2. Real part n and imaginary part k of the complex refractive index of the azo nickel chelate dye film (70 nm thick) in the visible region.

3.2. Spectroscopic properties of the azo nickel chelate dye films

The absorption spectrum of azobenzene exhibits three absorption bands in the visible and near-UV regions, assigned as n – π^*, π – π^* and ϕ – ϕ^* transitions [12]. The simple orbital diagram is shown in Fig. 4.

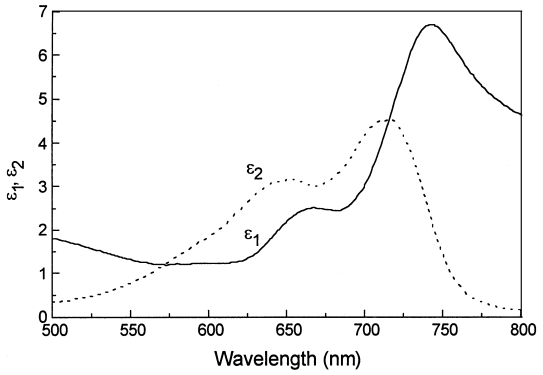

Fig. 3. Real part ε_1 and imaginary part ε_2 of dielectric function of the azo nickel chelate dye film (70 nm thick) in the visible region.

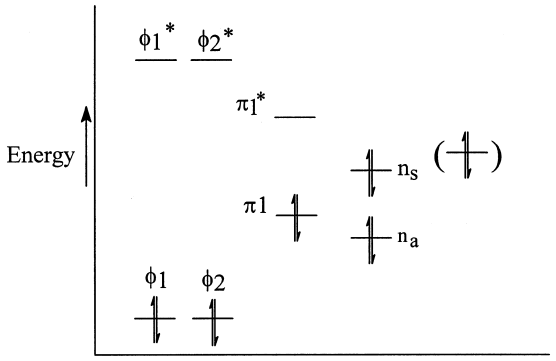

Fig. 4. MO energy diagram for the azo dye system.

The lowest-energy transition $n_s - \pi^*$ occurring at approximately 400–500 nm is partly forbidden, as indicated by the low intensity ($\varepsilon \sim 10^3$) and hypsochromic shift of the band in polar solvents. The $\pi - \pi^*$ transition is allowed and occurs at 300–400 nm ($\varepsilon \sim 10^5$). The band shows a bathochromic shift in polar solvents and is sensitive to substituent effects. The highest energy transition is due to $\phi - \phi^*$ transitions in the aromatic system, as well as in the heterocyclic rings. The transitions are regarded as localized in these rings, and the bands occur in the region at 200–300 nm. If the coupling component in the azobenzene system is substituted with electron donating groups, the $\pi - \pi^*$ band undergoes a large bathochromic shift, and consequently, the $n_s - \pi^*$ band can not be detected in the spectrum. The absorption band is then assigned as an $\pi - \pi^*$ transition. In the azo metal chelate compound (Fig. 1), one of the nitrogen atoms of the azo group with its sp^2 lone pair electrons, together with the nitrogen atom of the benzothiazole ring bonded to the nickel ion, gives a 5-membered chelate ring. The terminal sulfonic acid group forms an inner salt ($SO_3^-M^+$) of the metal chelate compound. The formation of such an inner salt by the terminal sulfonic acid group with the metal ion results in an increase of the electron-donating ability of the coupling component. Consequently, the energy of the $\pi - \pi^*$ transition is lowered. The absorption band of the azo metal chelate compound is significantly bathocromically shifted in comparison with the azo dye. Fig. 5 shows the absorption spectra of the azo dye and its nickel chelate compound in solution and in thin films. The spectrum of the azo dye (curve A) shows a peak at 559 nm($\varepsilon = 1.45 \times 10^4$) in methanol, and that the spectrum of its nickel chelate compound (curve B) is red-shifted and gives two peaks at 625 nm ($\varepsilon = 4.65 \times 10^4$) and 683 nm ($\varepsilon = 5.58 \times 10^4$), respectively. The absorption bands are further red-shifted to 640 and 706 nm due to molecular aggregation in the film (curve C). In addition, the electron deficient metal ion attracts electrons from the nitrogen atoms in the benzothiazole ring and the azo group, so that the electron density at the azo linkage is reduced. The electrophilic photo-oxidation attack at that position is retarded in the azo metal chelate compound. Thus, the lightfastness of the dye film is improved.

The absorption coefficient α can be calculated from the following relationship:

$$\alpha = 4\pi k/\lambda = 2\pi\varepsilon_2/\lambda n$$

Fig. 6 gives the plot of α vs wavelength.

Fig. 7 shows the transmission (T) and reflection (R) spectra of the 70 nm thick azo nickel chelate dye film on glass and the reflection spectrum with an additional aluminium reflective layer (R-Al). It is apparent that the reflectance of the azo nickel chelate dye film measured through the glass plate reaches a value of 33%, and increases to 58% with

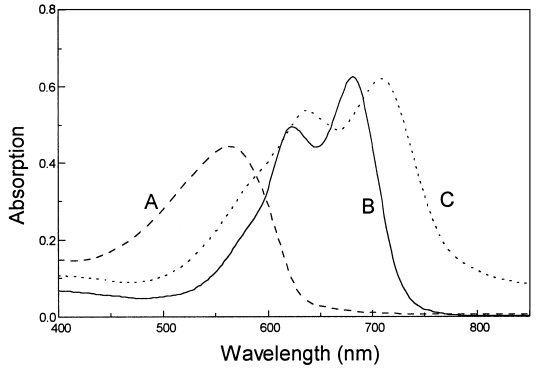

Fig. 5. Absorption spectra of the azo dye and its nickel chelate compound; A. Azo dye in methanol (3.10×10^{-5} mol·1^{-1}); B. Azo metal chelate dye in chloroform (1.13×10^{-5} mol·1^{-1}); C. Azo dye metal chelate film (70 nm thick).

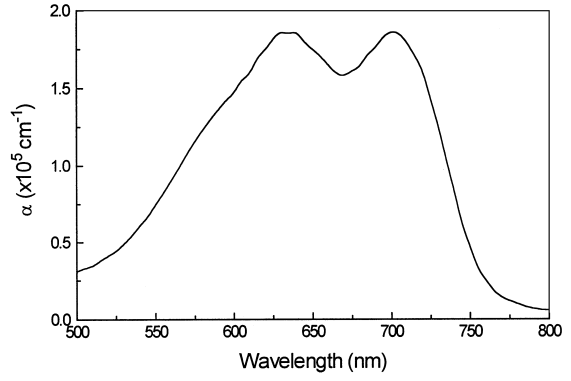

Fig. 6. Variation of absorption coefficient α vs wavelength of the azo nickel chelate dye film (70 nm thick).

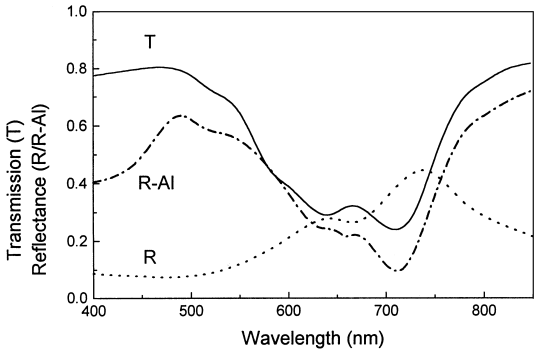

Fig. 7. Transmission and reflection spectra of the 70 nm thick azo nickel chelate dye film; T, Transmission; R, Reflectance without aluminium reflective layer; R-Al, Reflectance with an aluminium reflective layer (70 nm thick).

an additional aluminium reflective layer at 780 nm. It can be concluded that it could be useful as an optical recording medium.

3.3. Dynamic optical recording properties—a preliminary study

To examine the possible use of the azo nickel chelate dye film as an optical recording medium, we prepared multilayer films on a 12 cm polycarbonate substrate. The substrate was pregrooved with a track pitch of 1.6 μm and width of 0.6 μm. The dye film was fabricated by spin-coating on the substrate. Then, on the coating layer, a film of aluminium was deposited by the vacuum-sublimation method to form a reflective layer. Optical recording was performed by a dynamic optical recording tester utilizing signals of central frequency 500 kHz and duty ratio 6:4; the relationship of carrier-to-noise ratio (CNR), which is defined as the ratio of root mean square signal and root mean square noise, was obtained. The results indicated that CNR was 45 dB when the optical disc rotated with a linear velocity of 1.4 $m.s^{-1}$ and irradiated by 7 mW 780 nm semiconductor laser beam.

4. Conclusions

The azo nickel chelate compound prepared was highly soluble in organic solvents, so that it can be fabricated by the spin-coating method. An optical recording medium employing this compound showed good absorption and reflection properties. Dynamic optical recording tests showed that the azo metal chelate compound is a promising candidate for use in optical recording medium.

Acknowledgements

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