ELSEVIER

Dyes and Pigments 51 (2001) 93–101

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

The effect of solvent on the optical properties of cyanine dye films

Jun-Ping Zhang[a], Shu-Yun Zhou[a], Ping Chen[a,*], Okasaki Tsuneki[b], Hayami Masaaki[b]

[a]*Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100101, PR China*
[b]*Hayashibara Biochemical Laboratories Inc., NKR, Japan*

Received 7 March 2001; received in revised form 2 May 2001; accepted 10 August 2001

Abstract

In this paper, several cyanine dyes in different solvents were spin-coated onto glass substrates to form thin films. Vis-NIR spectra of reflection of the films were measured and optical constants (complex refraction index) were calculated. It was found the solvents could greatly affect the optical properties of dye films. Atomic force microscopy (AFM) was applied to observe the morphologies of the film surfaces and the results demonstrated that the reflectivity was closely related to the surface roughness of film. High surface roughness has a strong scattering effect on light and will lower the reflectivity. When tetrafluoro-propanol and chloroform were employed as solvents, the surface roughness of the film was low and high reflectivity was reliably obtained. © 2001 Published by Elsevier Science Ltd.

Keywords: Cyanine dye; Thin film; Optical properties; Solvent; Roughness, AFM

1. Introduction

Cyanine dyes [1–4] are the most popular information recording materials in CD-R and DVD-R optical disks. During the data writing process, the dye film, which is spin-coated on substrates, absorbs the laser beam energy and undergoes thermal deformation such as decomposition, evaporation or dissolution. The written data could be reproduced by reading the difference in reflectivity between the portions where such deformation was formed and those without such deformation. In order to decrease noise and increase credibility of data processing, dye film should have good optical properties.

In our previous papers [5–9], optical properties of several cyanine dyes have been studied and some dyes suitable for CD-R or DVD-R were found. In this paper, we found that the optical properties of dye films deposited from different solvents differed from each other. The morphological structure of the film surface was observed by AFM. It was shown that solvents greatly affected the roughness of dye films, resulting in the change of optical properties of the films, especially for their reflectivity. As we know, reflectivity is related to the CNR value, a key parameter in evaluating the quality and usability of optical discs [10,11]. Therefore, to select suitable solvents is very important in the process to fabricate dye films.

* Corresponding author. Tel.: +86-10-6488-8170; fax: +86-10-6487-9375.
E-mail address: chenlab@ipc.ac.cn (P. Chen).

PII: S0143-7208(01)00061-4

2. Experimental

2.1. Material

Molecular structures of the studied dyes provided by Nippo Shikiso Kenkysho Co. Ltd. are shown in Table 1, as well as their absorption maximum wavelengths (λ_{max}) and molar absorption coefficients (ε). According to the method described in our previous papers [8,9], the optical constants of dye films at different wavelengths of lasers were calculated from interference theory and listed in Table 1. Tetrafluoro-propanol with purity of 99% was purchased from Acros Organics. The other solvents (methanol, chloroform, diacetone alcohol) were analytical grade and purchased from Beijing Chemical Regent Factory. All compounds were used as received without further purification.

2.2. Methods

2.2.1. Film preparation

The dye films were fabricated through spin-coating method. In contrast to the usual spin coating of polymers, the time for solvent removal should be controlled less than 20 s so as to prevent the dyes from crystallizing into polycrystalline layers. This can be realized by using high spin rate (6000–10,000 rpm) and by using concentrated dye solutions. Solutions of dyes in different pure solvents and mixed solvents were coated on to glass substrates (26×26 mm). Since the optical properties of dye films are related to the thickness of the dye films, proper control is required in order to obtain similar thickness for different films. The solution concentration for D-1 is 2.8×10^{-2} mol/l and for D-2 is 6.9×10^{-2} mol/l.

2.2.2. Measurement of film thickness

The amount of dye spin-coated on substrate was determined by dissolving the whole film in a defined volume of methanol, followed by adsorption measurement of the dye solution. The film thickness can been calculated on the condition that the dye density has been known.

2.2.3. Measurement of optical properties

Absorption and reflection spectra of dye films were obtained by a Hitachi U-3000 UV–vis spectrometer with 5° incidence onto sample surface for reflection spectrum.

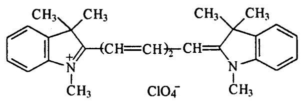
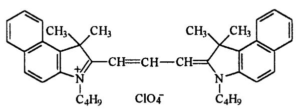
2.2.4. Measurement of FT–IR

The FT–IR spectra of dye powder in KBr compressed powder and dye film on silicon were collected with BIO RAD 165 Fourier-transform spectrometer at a resolution of 4 cm^{-1}.

2.2.5. AFM observation

The morphological structures were observed with SPE-400 (Japan) on T-mode. The surface roughness of the dye films were observed with a Nanoscope IIIa (Digital Instruments) scanning probe microscope with a multi-mode head in air. The AFM images of the samples were observed using T-mode with a silicon cantilever (resonance frequency ca. 300 kHz). For each sample, at least three areas were imaged and the same results were obtained.

Table 1
The molecular structures and optical properties of cyanine dyes

Abbreviation	Structure	λ_{max}[a] (nm)	ε[a]	Opt. const.[b] ($n+k$i)	$\lambda_{recording}$ (nm)
D-1		639	2.08×10^5	2.60 + 0.11i	780
D-2		588	9.26×10^4	2.16 + 0.07i	650

[a] Solution (in methanol).
[b] Film.

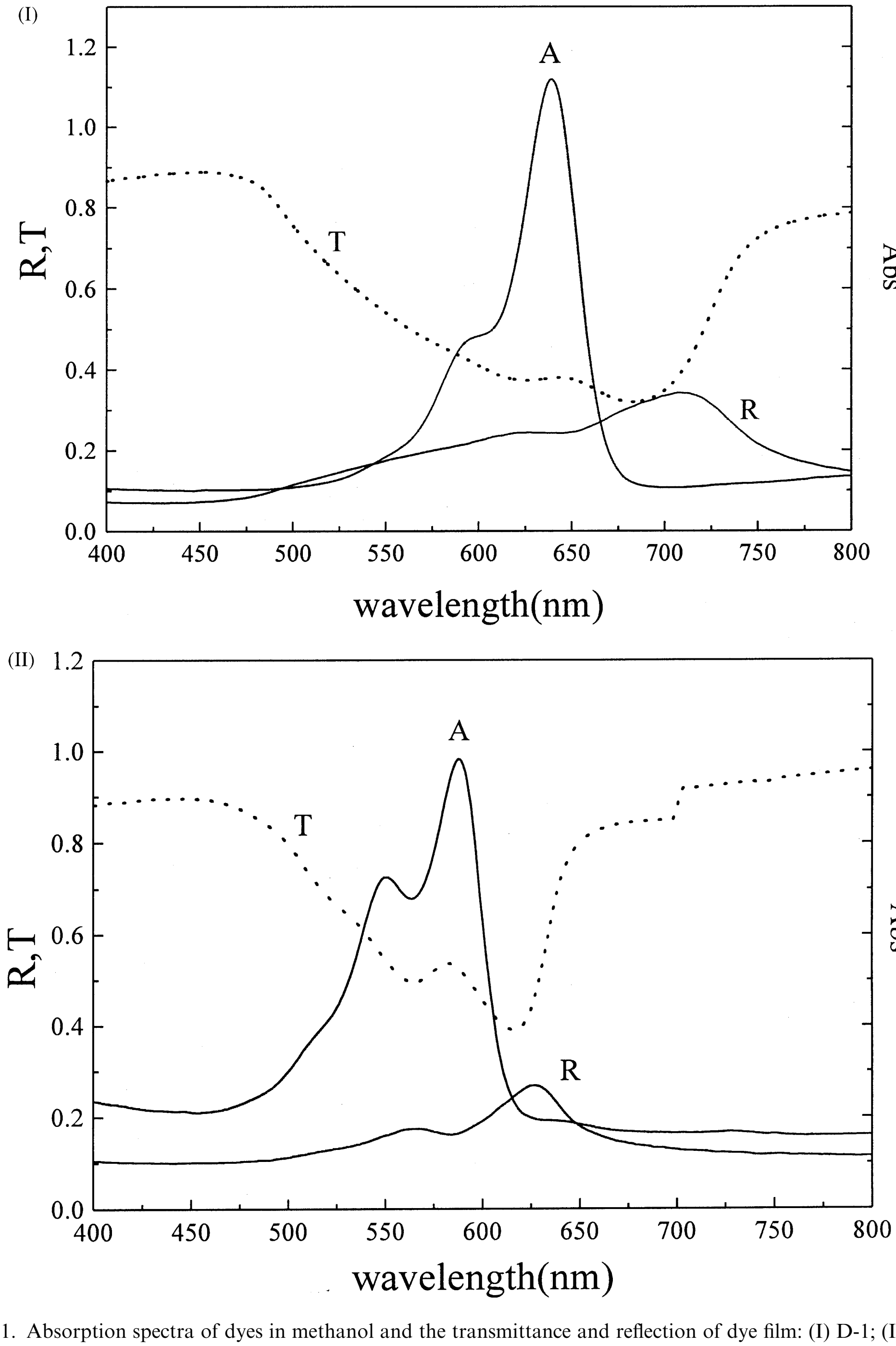
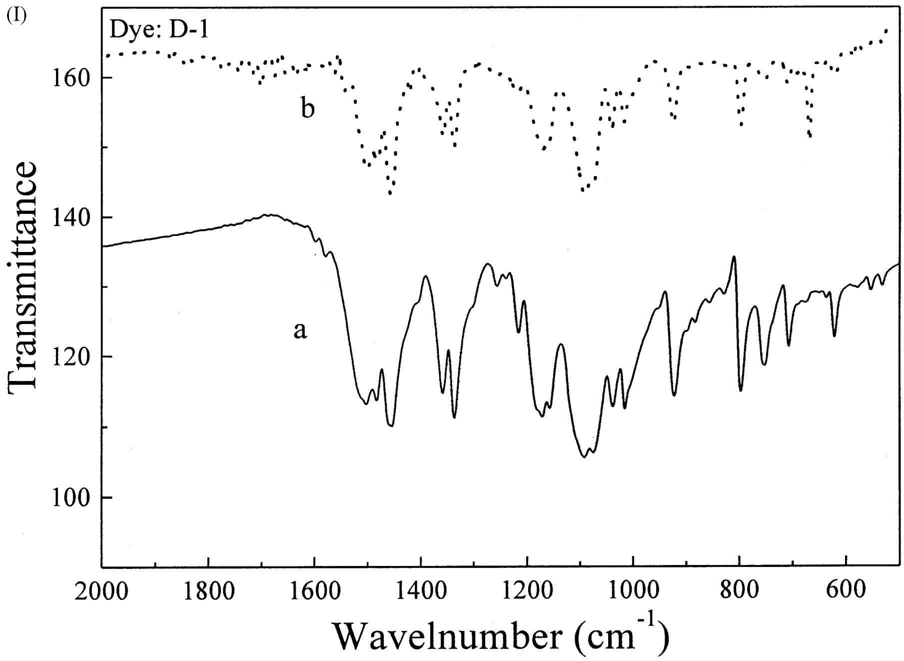


Fig. 1. Absorption spectra of dyes in methanol and the transmittance and reflection of dye film: (I) D-1; (II) D-2.

(I)



(II)

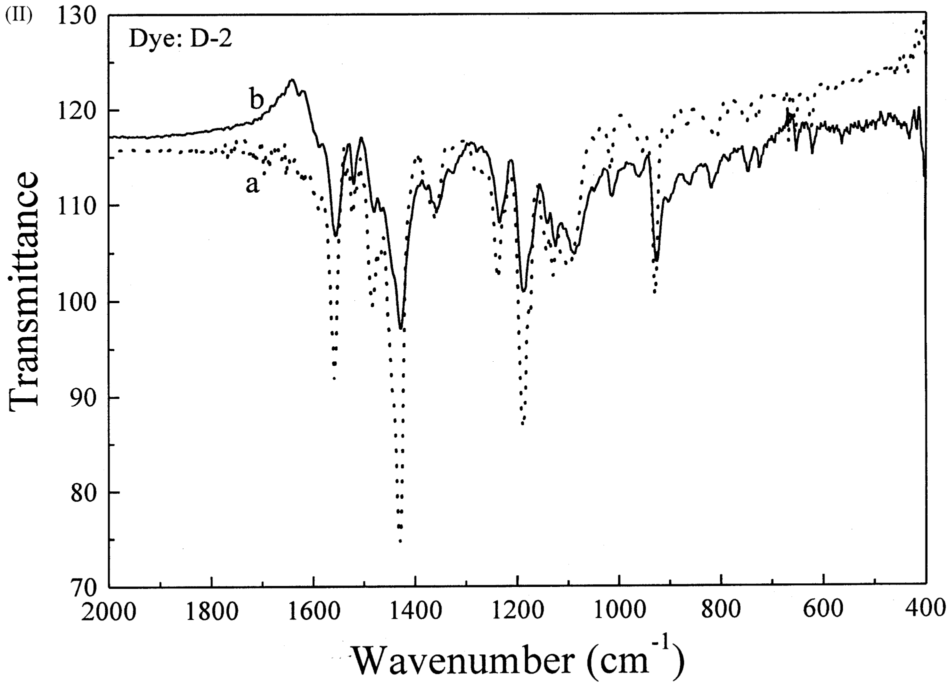


Fig. 2. IR spectra of the powder (a) and thin film (b) deposited from tetrafluoro-propanol: (I) D-1; (II) D-2.

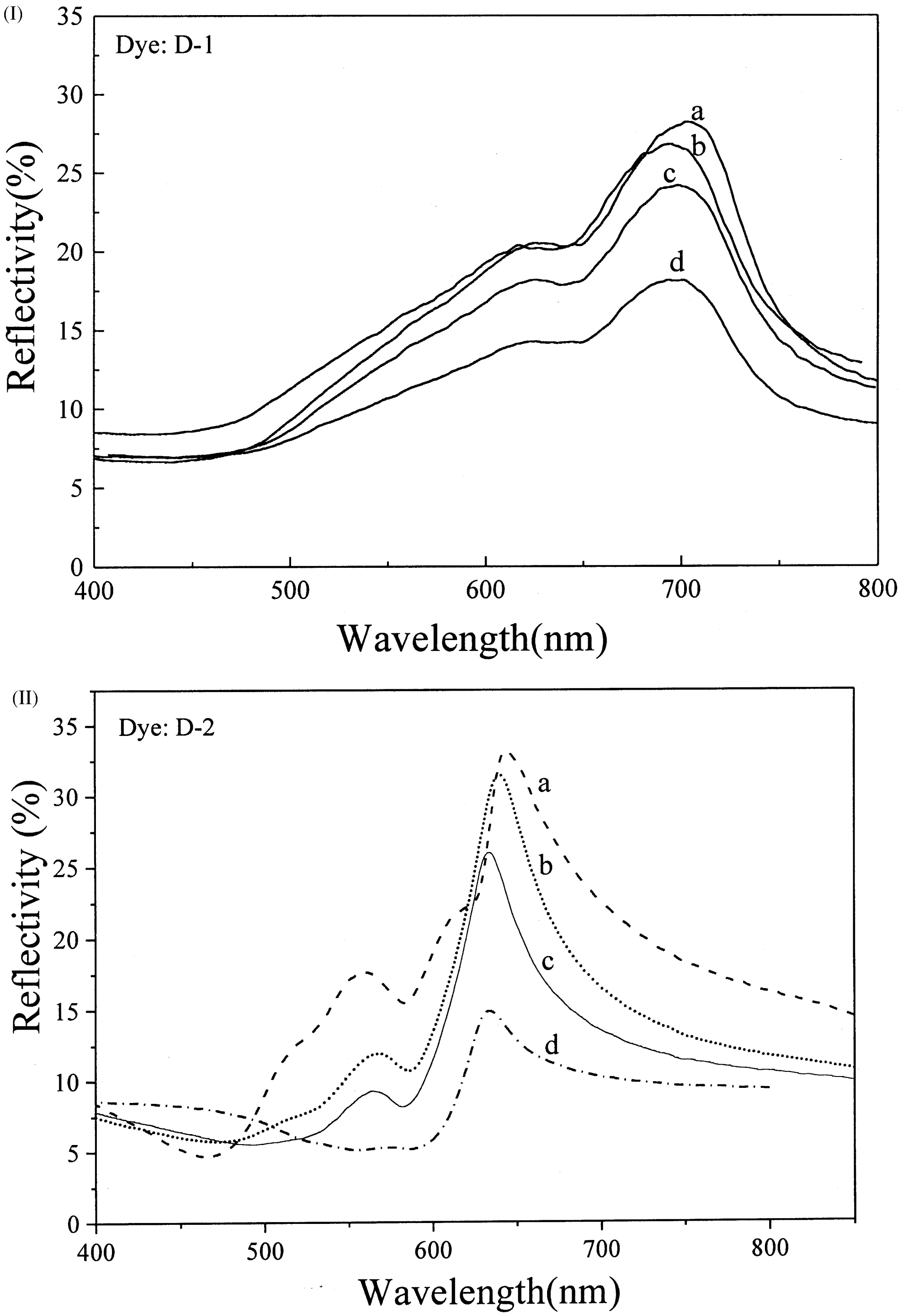


Fig. 3. The reflection of D-1 and D-2 films deposited from different pure solvents: (a) chloroform; (b) tetrafluoro-propanol; (c) diacetone alcohol; (d) methanol: (I) D-1; (II) D-2.

3. Results and discussion

3.1. The spectrum characteristics of cyanine dyes

Fig. 1 shows the absorption spectra (A) of dyes in methanol and their reflection (R), transmittance (T) for a 20 nm thick dye film in vis–NIR wavelength region. The absorption spectrum of the D-1 (Fig. 1I) in solution has a sharp peak at about 640 nm, the maximum value of the reflection spectrum shows a broad peak at around 700 nm, it is red-shifted compared with the spectrum of the same dye in solution. Such phenomena also can been found in that of D-2.

The FT–IR spectra in the function regions (400–2000 cm^{-1}) of dye powder (a) and films fabricated with tetrafluoro-propanol (b) are illuminated in

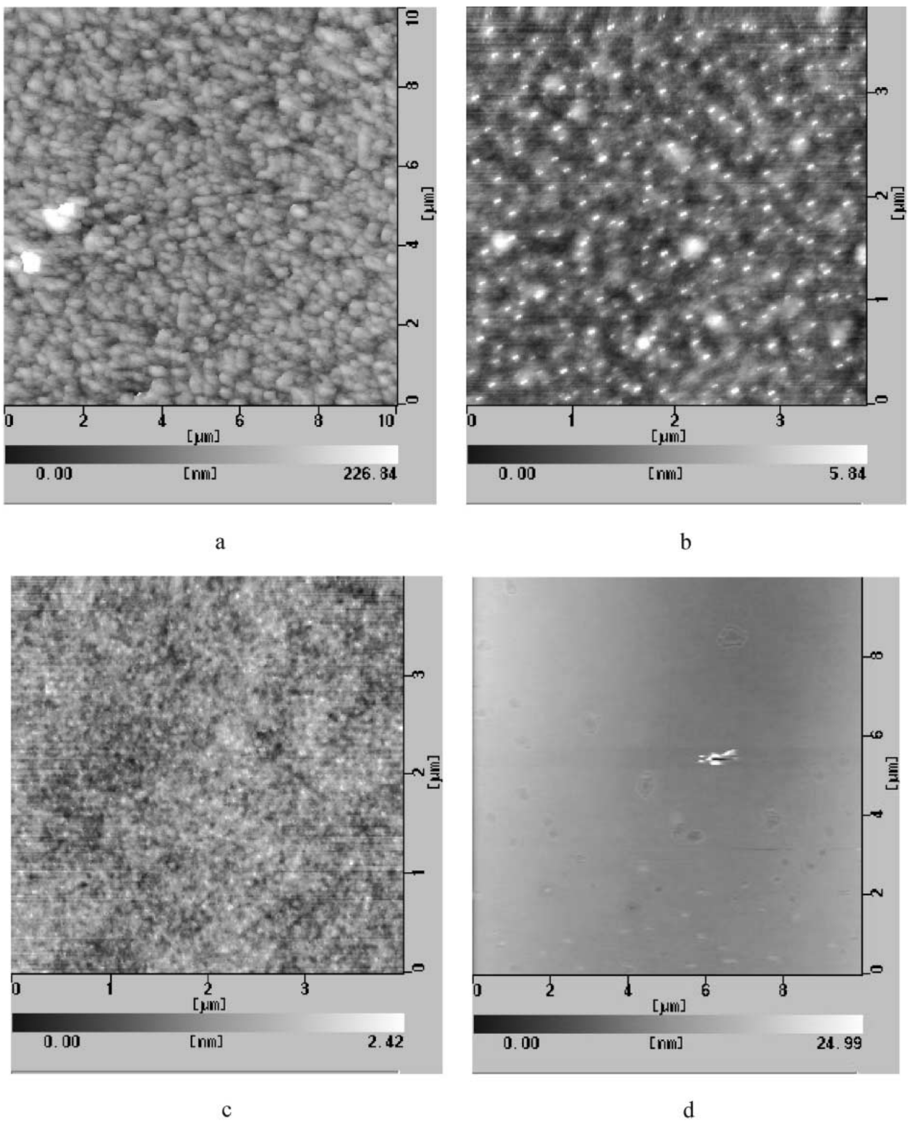
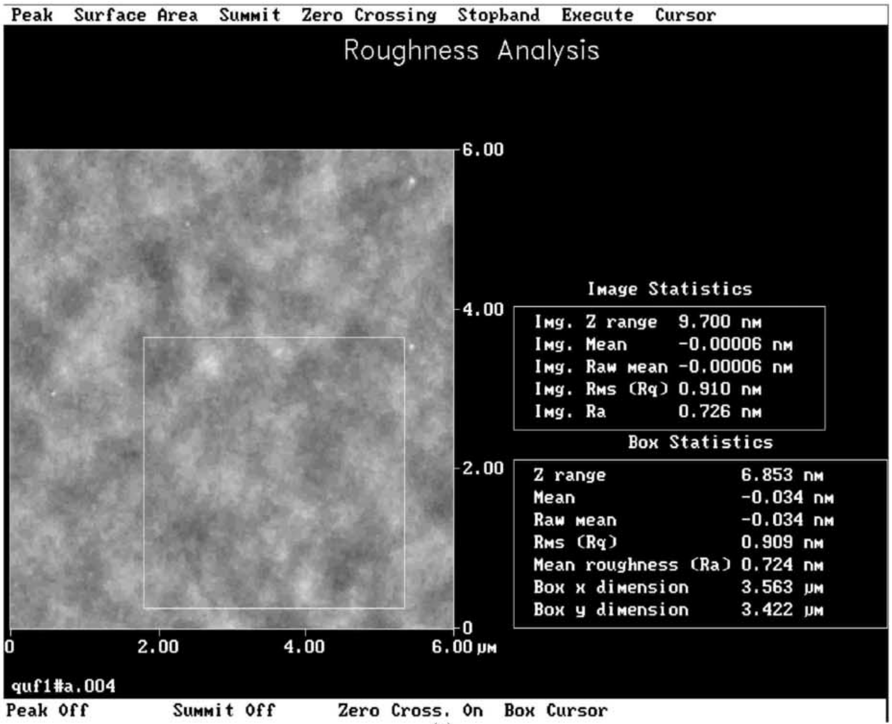
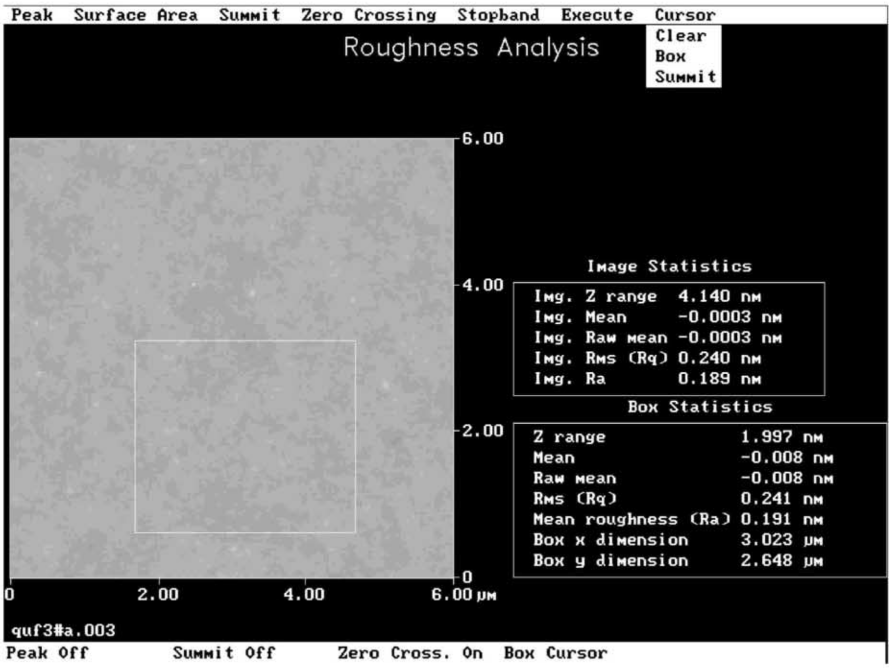


Fig. 4. The AFM photos of D-2 films spin-coated from different pure solvents. (a) methanol; (b) diacetone alcohol; (c) tetrafluoro-propanol; (d) chloroform.



(a)



(b)

Fig. 5. The images of the surface roughness of D-1 films observed by AFM: (a) diacetone alcohol; (b) chloroform.

Fig. 2. It is clear that there are no noticeable changes among the characteristic peaks of the thin film and those of the powder, which demonstrates that the solvents have no effect on the stability of the dye structure, same result as was ever reported by Gu [11].

3.2. The optical properties of dye films

To be compatible with the DVD-R player, dye film is required to has high reflectivity. In our experiments, after having compared the reflectivity of dye films formed in different pure solvents and mixed solvents, we found that the maximum reflectivity of these films were quite different.

The reflection spectra of D-1 and D-2 films fabricated with different pure solvents were illuminated in Fig. 3. It can be seen clearly that the reflectivity of D-2 films fabricated with chloroform and tetrafluoro-propanol are very high, near to 35%, and the next is diacetone alcohol. The film's reflectivity is the lowest (only 15%) while using methanol as solvent, just about 15% (Fig. 1II). As we know, the effects of solvents on the optical properties of dye film has not been reported up to now.

We also studied the effect of mixed solvents on optical properties of dye films. The maximum absorption and reflectivity were exemplified in Table 2. It can be seen obviously that the films exhibit different reflectivity owing to different volume ratio of the mixed solvents. When fabricated with the mixture of diacetone alcohol and chloroform (volume ratio 5:5), D-1 film showed the maximum reflectivity up to 31.9%, higher than those at other mixture ratios. As for D-1 and D-2 film, their reflectivity both reached to the maximum value while the mixture volume ratio of diacetone alcohol and tetrafluoro-propanol was 3:7.

Table 2
The reflectivity and absorption of dye films fabricated in various mixed solvents

Volume ratio of mixed solvents		1:0	7:3	5:5	3:7	0:1
D-1[a]	Reflectivity (%)	18.2	24.2	31.9	20.5	28.2
(20 nm thick)	Absorption (%)	28.2	30	–	36.9	25.0
D-2[b]	Reflectivity (%)	17.0	24.3	24.3	27.3	22.6
(45 nm thick)	Absorption (%)	26.6	28.0	23.4	26.2	24.0
D-1[c]	Reflectivity (%)	18.2	20.1	23.8	24.5	23.3
(20 nm thick)	Absorption (%)	28.2	33.2	28.2	23.1	22.2

[a] Diacetone alcohol:chloroform.
[b] Diacetone alcohol:tetrafluoro-propanol.
[c] Diacetone alcohol:tetrafluoro-propanol.

Table 3
The surface roughness of dye films fabricated with various solvents

Dye film	Solvent	Box statistics	
		Rms (R_q) (nm)	Mean roughness (R_a) (nm)
D-1	Diacetone alcohol	0.909	0.724
	Tetrafluoro-propanol	0.276	0.220
	Chloroform	0.241	0.191
	Methanol	27.86	21.42
D-2	Diacetone alcohol	0.889	0.617
	Tetrafluoro-propanol	0.301	0.239
	Chloroform	0.202	0.161

3.3. AFM observation for dye films

The morphologies of the dye films formed with different solvents were observed by AFM, as shown in Fig. 4. It is obvious that there are great difference among the films. For the dye film fabricated with methanol, the surface was very rough, and dye crystalloid was formed. While using diacetone alcohol as solvent, there was also obvious particulate appeared, but the surface was less roughish. The films became much even when made from tetrafluoro-propanol and chloroform, respectively.

Fig. 5 gives the corresponding photos of the surface roughness. As shown in the figures, the mean roughness are various while with different solvents. Table 3 lists the data of their roughness. These results demonstrated that chloroform and tetrafluoro-propanol are relatively favorable solvents for the cyanine dyes in CD-R and DVD-R.

From the results observed by AFM and the reflection spectra in Fig. 3, we can infer the change of reflectivity to the different morphological roughness. As shown in the Fig. 4, the film fabricated with methanol is composed of closely piled micro-crystal particles sized 0.3 μm, which have strong scattering effect on incident light resulting the decrease of the reflectivity. If the surface of the dye film is very even, there is no scattering and relative high reflectivity can be obtained. The explaination was strongly supported by the excellent agreement between the roughness in Table 3 and reflectivity spectrum in Fig. 3.

The AFM results clearly show that the solvents is a significant factor influencing the morphology and roughness of dye film. The main reasons might be as follows: For a cyanine dye, each solvent has its special solubility, polarity, viscosity, volatility and so on. During the spin-coating, those above factors would affect the dye deposition from solution, resulting in the change of the film's morphological structure.

4. Conclusion

The optical properties of cyanine dye films fabricated in different pure and mixed solvents had been measured. The morphologies and roughness of films were observed by AFM. Results showed that surface roughness markedly affect reflectivity, the more even the film surface is, the higher the reflectivity will be. It can be concluded that selecting suitable solvents for recording layer is of great importance in disc fabrication process.

Acknowledgements

The authors would like to acknowledge the National Natural Science Foundation of China (grant No. 69848002) for financial support of this work, and the authors would also thank Professor Jiang Lei and Dr. Qu Xiao-zhong (Institute of Chemistry, Chinese Academy of Sciences) for their kind assistance on AFM test.

References

[1] Gravesteijn DJ, Veen J. Philips Tech Rev 1983;41:325.
[2] Ferreira LF, Oliveira AS, Wilkinson F, Worrall D. J Chem Soc, Faraday Trans 1996;92(7):1217.
[3] Christian R, Ulrich B. Liebigs Ann 1995;329.
[4] Emiko H, Toru F. Jpn J Appl Phys 1997;36:593.
[5] Sun S, Chen P, Zheng D, Okasaki T, Hayami M. The Imag Sci J 1998;46:99.
[6] Li J, Chen P, Zhao J, Zheng D, Okasaki T, Hayami M. Chin Chem Lett 1997;11:8.
[7] Zhao J, Chen P, Li J, Zheng D, Okasaki T, Hayami M. J Photochem 1997;59:15.
[8] Sun S, Chen P, Zhou S, Zheng D, Okasaki T, Hayami M. The Imag Sci J 1997;47:113.
[9] Sun S, Chen P, Zheng D, Okasaki T, Hayami M. SPIE 1997;3562:11.
[10] Chen Q, Gu D, Gan F, Xu L, Li M. Appl Surf Sci 1996; 93:151.
[11] Gu D, Chen Q, Shu J, Tang X, Gan F, Shen S, Liu K, Xu H. Thin Solid Films 1995;88:257.