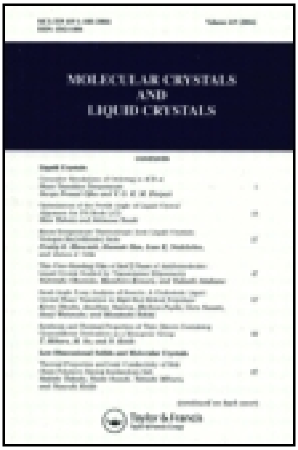

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Optical Properties and Application of Photochromic Diarylethene

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Optical Properties and Application of Photochromic Diarylethene

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The optical properties of cis-1,2-dicyano- 1,2-bis(2,4,5-trimethyl-3-thienyl) ethene as a photochromic dye is studied. Vacuum evaporation has been used to prepare thin films for possible practical applications, especially optical information storage.

Keywords: Photochromism; optical properties; application

INTRODUCTION

To meet the growing demands for high-speed and high-density data processing, continuing efforts are being devoted to increase the recording density of optical data storage [1]. Various approaches have been proposed to increase the recording density: reduction of the recording mark size(shorter wavelength lasers, super-resolution and near-field optical recording), three dimensional recording, multiple-wavelength recording, and improvement in coding [2,3]. As one group of materials of great importance, organic materials exhibit several unique advantages including rapid response, tremendous variety, low cost, and possibility of easy fabrication.

Among various organic materials, photochromic materials are very promising [4-6]. Besides optical data storage, their potential applications in holographic storage and optical switching devices have also received great attention [7,8]. Various photochromic dyes have been proposed to improve their photochromic properties such as reversibility and stability. Unfortunately, photochromic properties have been studied in the solution phase and the preparation of high quality thin film seems to be difficult in many cases. As a new type of photochromic material, diarylethene derivatives have been recently reported to be fatigue resistant and thermally irreversible photochromic compounds with promising potential for applications [9,10]. However, details about their physical and chemical properties are still insufficient.

In this study, one of diarylethene derivatives, cis-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl) ethene (CMTE) is investigated. Kawai and Yoshino *et al.* studied the optical and dielectric properties of the dye in amorphous state and its applications including photoluminescence performance [11-14]. They prepared the sample by melting the CMTE powder at temperature higher than 120℃ under an argon gas atmosphere and forming a thin layer from the viscous liquid state by rapid cooling within a cell of two quartz substrates and Telflon spacers through capillary action. Other alternative methods are being investigated including dispersion of dye into the polymer matrices by vapor-transport method [15]. These techniques involve the treatment of the dye and substrate at increased temperatures which are undesirable in many applications. To prepare thin films of the dye by convenient, low cost techniques is extremely attractive for applications. In this study, thin films of CMTE have been prepared by vacuum evaporation. The optical properties of CMTE in dilute solutions and condensed phases are measured as well as its photochromic process upon UV and visible light irradiation.

EXPERIMENTAL DETAILS

In this study, commercial products of CMTE from Tokyo Kasei Chem. Ind. was used. The CMTE thin films were prepared by vacuum evaporation on quartz substrates at a pressure low than 10^{-4} Pa using a Knudsen cell as the evaporation source. The thin film preparation conditions were carefully selected and the deposition rate was about 0.16 nm/s. Thin film thickness was measured on a Dektak Surface Profile Measuring System (Sloan Technology, Veeco Instrument Inc.).

The absorption spectra of CMTE in solution were obtained from UV-2200 UV-VIS recording spectrophotometer (Shimadzu Co., Japan). Measurement of the optical properties of the thin films was performed on a spectrophotometer with multi-channeled photo detector (PMA-11, Hamamatsu, Japan). For the photoisomerization experiment, an UV lamp of wavelength 365 nm was adopted with irradiation intensity 0.56 mW/cm^2 (Ultra-violet Products, Inc, CA, USA) as the UV light, while tungsten lamp light after a yellow filter was used for the irradiation of visible light. The morphology of the CMTE thin films was observed by contact-mode atomic force microscopy (SPI3800, Seiko Instrument, Inc.).

RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra of CMTE in ethanol where an absorption peak at 522 nm upon UV light irradiation can be found (closed-ring form). This absorption peak disappears after yellow light irradiation (open-ring form). The process is a reversible photochromism between the closed-ring form and open-ring form of the CMTE molecules. In photoirradiation process, the open-ring form CMTE molecules absorb the irradiated UV light and the excited molecules change to the closed-ring form isomers which are absorptive around 522 nm. By using different solvents, similar spectral change could also be found for two isomers during the photochromic process. The peak wavelength of the closed-ring form of the CMTE molecules exhibits blue-shifted for low concentrations and discrepancy for different solvents, which is probably due to the polarity effect of the solvent and molecules (Fig. 2).

The vacuum evaporated CMTE thin films also show pronounced photochromic features, as shown in Fig. 3. There is a strong absorption peak around wavelength 400 nm for the thin film. Instead of a sharp absorption peak in the spectra of solution, an absorption shoulder appears in the wavelength region of 450-610 nm centered at 530 nm for CMTE thin film after UV light irradiation with the transmittance of the thin film changes from 0.50 to 0.35 at 530 nm. CMTE thin film on the quartz substrate was found to be in the polycrystalline state. Morphology of an CMTE thin film of about 1.5 μm in thickness on quartz is illustrated in Fig. 4. Observation of the morphology of thin films of different thickness indicates that the molecules grow in island structure. Minute granules as small as 200-300 nm in diameter may agglomerate to form islands of micron size. During the evaporation process, separate islands may connect to each other and pile up. No morphology change was identified by AFM during the reversible photochromic process. The morphology was observed to be stable at least for several months.

As an example of the application of the photochromism of the thin film, photoimage formation has been realized on the vacuum evaporated CMTE thin films. By irradiating the CMTE thin film by UV light through a mask, the molecules in the irradiated areas may be turned to the closed-ring form of red in color. In this case, the irradiated CMTE molecules possess different optical properties (absorption) in contrast to those without irradiation and fulfill the information storage. In the same way, it is also possible to use the optical properties of the open-ring form for information storage. The process here is reversible. Despite the scale, the recording mechanism here is in principle the same as that of the near-field optical recording on the thin film. The photoimage formation was reported for the amorphous thin films prepared by the technique mentioned above [11].

CMTE thin film exhibits absorption peak around 400nm (Fig. 3), which reminds us the possibility of its application as a recording medium in next-generation short-wavelength recording. It is well known that blue laser will be adopted in the optical memory devices in the near future, which will greatly increase the storage density over current 630-640 nm semiconductor lasers. CMTE thin film with aluminum overcoat shows considerable reflectivity change after 400 nm semiconductor diode laser irradiation as depicted in Fig. 5. The relative reflectivity change increased from 0.12 to 0.52 when the laser power increased from 0.08 to 0.83 mW. The trends appear to be nearly linear. On the other hand, photochromic thin films as super-resolution media in ultra-high density storage is also very promising, which requires further study on the nonlinear transmission change of the thin films.

CONCLUSIONS

Photochromism of cis-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl) ethene in dilute solution and condensed phase has been studied. Reversible transformation of the molecules between open-ring form and closed-ring form can be initiated by the irradiation of UV and yellow light accompanying the change of absorbance around 522 nm in solution. Of particular importance is the successful preparation of thin film by convenient vacuum technique with pronounced changes of the optical properties in the photochromic process, which may find important application as recording medium or super-resolution medium in high density data storage.

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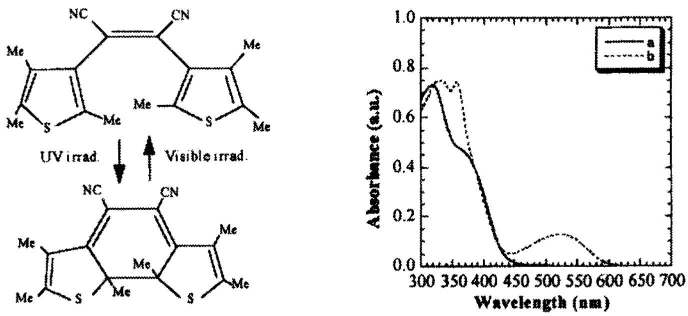

FIGURE 1 Schematic illustration of the photochromism of CMTE and the absorption spectra of CMTE in ethanol: a, after yellow light irradiation; and b, after UV light irradiation.

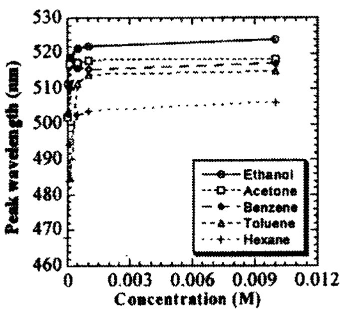

FIGURE 2 Concentration dependence of the absorption peak wavelength of the closed-ring form CMTE in different solvents.

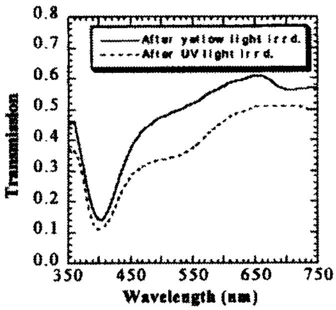

FIGURE 3 Transmission spectra of CMTE thin film (1.5 μm).

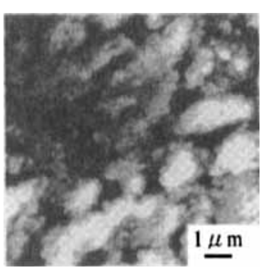

FIGURE 4 AFM image of an as-deposited CMTE thin film (1.5 μm).

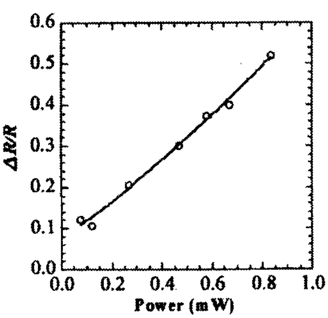

FIGURE 5 Relative reflectivity change of CMTE thin film (814 nm) with Al overcoat after 400nm laser irradiation.

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