A Formation of Organic Rewritable Optical Memory Media Using the Vapor Transportation Method

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1. Introduction

Organic molecules have been widely used in production of opto-electronic devices, such as liquid crystal displays (LCD), compact disks-recordable (CD-R) media, electro-luminescence (EL) devices,^{1–3} thin film transistors,^{3,4} solar cells,^{1,5} etc. Methods using an organic thin film and/or a thin layer are the important techniques used in the production of these devices with complex structures, but there are many problems with the present methods. The vacuum vapor deposition process, which is used for compounds with high vapor pressure, is widely used, but organic compounds make some decomposition during the evaporation process. Wet processes with organic solvents such as casting and spin-coating are more commonly used for the formation of organic thin films. However, it is difficult to remove residual solvent molecules from films, the thicknesses of which are over 500 nm. Small amounts of residual solvent in the films often cause Rayleigh scattering or convert into the gas phase, causing small cracks after heating by application of bias voltage or by irradiation with focused light.^{6,7}

The “vapor transportation method” with vacuum technique^{8,9} is one of the most useful methods to resolve these problems. A polymer “thin” layer with “densely dispersed” organic molecules of low molecular weight can be formed easily using this method under high vacuum. Moreover, dispersion of photochromic compounds including *cis*-1,2-Dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl) ethene (CMTE) into a polymer matrix achieves a photochromic reaction: that is, the

present method is an interesting method for the formation of an organic thin layer, which can attach characteristics of CMTE molecules to polymer surfaces. In this study, we investigated differences in formation rates between polystyrene (PS), polycarbonate (PC) and poly(methyl methacrylate) (PMMA) thin layers with densely dispersed organic photochromic dyes using the “vapor transportation method” at various temperatures. These differences have also been developed to allow fabrication of CMTE-containing nano-domains in the surface region of PS-*block*-PMMA (PS-*b*-PMMA) films with micro phase separation structures, observed by energy-filtering transmission electron microscopy (EF-TEM).^{10–14} Films with CMTE-containing nano-domains can be used as high-density memory media for optical recording when used in combination with the technique of scanning near field optical microscopy (SNOM).^{15–19}

2. Experiments

CMTE, which is a derivative of diarylethene,²⁰ was prepared as a model photochromic compound in this study. CMTE was obtained from Tokyo Chemical Industry Co., Ltd., and was used without further purification. Polymer pellets of polystyrene (PS; Aldrich Chemical Co., Inc., M_w : 280,000), poly(methyl methacrylate) (PMMA; LP-1®, Asahi Kasei Co., Inc., M_w : 140,000 ~ 150,000), and polycarbonate (PC; Aldrich Chemical Co., Inc., M_w : 64,000) were prepared for the present experiment. Polymer

Fig.1. Cross-sectional view of CMTE-containing PS layer after UV light irradiation

pellets (diameter ~ 2.5 mm, length ~ 3 mm) were introduced into Pyrex glass tubes with a small amount of powder of CMTE (5 mg), and the pressure in the tube was reduced using a vacuum pump^{8,9} (base pressure: 2×10^{-6} Pa). After reaching the base pressure, the glass tubes were sealed by melting to form ampoules. These ampoules were heated uniformly at temperatures ranging from 80°C to 120°C. Polymer layers and/or films containing CMTE were obtained in the surface region of the polymer substrate.

For analysis of the depth and the interface structure of the CMTE-containing region, CMTE was dispersed into polymer pellets, which were then cut into sections using razor-edges. After UV irradiation ($\lambda_{\text{max}} \sim 360$ nm) for 10 minutes, cross-sectional views of the samples were examined using an Olympus BH2-RFCA optical microscope.

3. Results and Discussion

Fig.1 shows cross-sectional view of PS pellet in which CMTE was dispersed using the vapor transportation method at 105°C for 172 h. After UV irradiation, CMTE in these polymer pellets was transformed from an open-ring to a closed-ring form, resulting in photoisomerization of CMTE:²¹ that is, the color of CMTE-containing layers changed from light yellow to red-brown. This indicated that the present method resulted in attachment of the specific characteristics of CMTE molecules to the polymer surfaces with ease of processing and handling. For diarylethenes, including CMTE, which have the advantages of thermal irreversibility, fatigue-resistance, and high sensitivity,²⁰ the present method is effective for fabrication of optical devices, such as memory media for optical recording and optical switching

devices. These figures also illustrate that CMTE-dispersed layers were formed uniformly perpendicular to the surface, and that the interfaces between polymer layers containing CMTE and substrates had a step structure. We are currently analyzing the structures of the interfaces in detail by microspectrophotometry and will present these results in a future paper.

Fig.2 shows the depths of CMTE-dispersed regions of PS pellets as a function of the duration of heat treatment at temperatures ranging from 85°C to 110°C. The formation rates of polymer thin layers with densely dispersed CMTE using the vapor transportation method largely increases with an increase in the treatment temperature: the thickness of the CMTE-containing PS layer formed after heating for 240 h were 0.024 mm and 0.28 mm at 95°C and 110°C, respectively. This result also indicated that the depth of the CMTE-dispersed region was determined by both treatment time and temperature. It was already found that the saturated concentration of films containing CMTE and another organic molecules with low molecular weight made by the present method,^{22,23} was dependent on the treatment temperature, indicating that the saturated concentration can be controlled by the treatment temperature. Thus, it is better to control the depth of CMTE-dispersed regions by the treatment time. Moreover, the present method is efficient for industrial use of formation of thin polymer films and/or layers containing organic functional molecules in a short time: it took only 20 minutes for formation of the CMTE-dispersed region of PS, the thickness of which was around 1 μm at 110°C.

Fig. 2 Depth of CMTE-dispersed regions of PS as a function of the duration of heat treatment at 85°C (closed circles), 95°C (open triangles), 105°C (closed diamonds) and 110°C (open squares), respectively.

Figs.3(a) and 3(b) show depths of CMTE-dispersed regions of PS (closed circles), PMMA (closed squares), and PC (open triangles) pellets as a function of the duration of heat treatment at 110°C and 95°C, respectively. The rate of formation at both 110°C and 95°C was as follows: PS > PC > PMMA. This result indicated that the differences in formation rate between PS, PC and PMMA were largely dependent on the treatment temperature. It is reported that percentages of water absorption of PS, PC and PMMA are as follows: PS < PC < PMMA,²⁴ indicating that hydrophobic properties are as follows: PS > PC > PMMA. Thus, these differences were largely dependent on an "affinity" to organic molecules, including CMTE, of these polymers.

These differences have also been developed to allow fabrication of CMTE-containing nano-domains in the surface region of PS-*block*-PMMA (PS-*b*-PMMA) films with micro

phase separation structures,²⁵ observed by EF-TEM.¹⁰⁻¹⁴ If observation and photoisomerization of the CMTE-containing nano-domains (diameter ~ 20 µm), the absorption or transmittance of which can be converted by the photochromic reaction, can be achieved using the SNOM technique,¹⁵⁻¹⁹ micro phase separation films such as PS-*b*-PMMA with CMTE-dispersed nano-domains will be applicable for rewritable optical recording systems with ultra-high density in the future.

4. Conclusions

Thin layers of CMTE-dispersed polymers (PS, PMMA, PC) were formed using the "vapor transportation method." The present method is an efficient method for the formation of organic thin films or layers that can easily attach the specific characteristics of CMTE molecules to polymer surfaces. The rates of formation of the CMTE-containing layer largely increases in the treatment temperatures and were as follows: PS > PC > PMMA. The differences in the formation rates between polymer matrices can lead to selective dispersion of organic molecules of low molecular weight into the PS nano-domains of the PS-*b*-PMMA film, resulting in the addition of functional characteristics of these molecules to nano-structures in the polymer surface region for application as high-density memory media for optical recording.

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Fig. 3 Depth of CMTE-dispersed regions of PS (closed circles), PMMA (closed squares), and PC (open triangles) pellets as a function of the duration of heat treatment at 110°C [plot (a)] and 95°C [plot (b)].

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