Thermal Decomposition and Deformation of Dye and Polycarbonate in Compact Disc-Recordables

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(Received March 31, 1997; accepted for publication September 3, 1997)

The thermal decomposition and deformation of a compact disc-recordable were simulated and observed. From the calculation, the writing power for the dye melting, dye decomposition and the polycarbonate (PC) deformation was predicted, and was experimentally confirmed by atomic force microscopy (AFM) observation of the dye layers and PC substrate. The deformation effects of each layer were evaluated according to the recording characteristics, the laser to noise ratio (CNR). In the writing power range of 4.0-6.0 mW, the deformation of the PC substrate contributes to the CNR increase and the 7α plays an important role in efficiently improving the CNR.

KEYWORDS: optical recording, compact disc-recordable, thermal deformation, thermal decomposition

1. Introduction

Recently, there has been a great deal of interest in the development of suitable organic materials for use in high density optical storage. Although several metal alloy systems have been studied for practical use in phase change optical media and magnetic-optical media, organic materials have been considered as the ideal optical media due to advantages in writing efficiency, fabrication cost and stability.

More recently, a compact disc-recordable (CD-R) using organic dye attracted considerable attention and it is now undergoing explosive growth because of its compatibility with compact disc (CD) format and the strong demand for economical high-capacity storage. A CD-R is a representative optical recording medium with the advantages of organic materials. It consists of a polycarbonate (PC) substrate, an organic dye layer, a gold reflective layer and an UV-cured resin overcoat (Fig. 1). It requires relatively low writing power and a simple spin coating process for fabrication. Previous research has reported that the recording mechanism in the CD-R is the deformation of each layer and that these deformations are damped at the dye layer. The deformation is recorded using various microscopic techniques. The structure of a CD-R and its possible deformation effects discussed in earlier papers are shown in Fig. 1. As shown in the figure, the three deformations are recorded as the focused signal and contribute to form an appropriate signal. No research has elucidated the effects of each deformation, and most research work has concentrated on only the observation of the deformation in the CD-R consists of thin film and therefore, it is quite difficult to separately observe the deformations of the dye layer and the PC substrate.

In this paper, the thermal decomposition and deformation effects of the dye layer and PC substrate were investigated by numerical analyses and actual experiments. To compare the calculation and experimental results, a CD-R with a glass substrate and a CD-R with a PC substrate were made and their deformations and recording characteristics were studied.

2. Engineering Analysis

2.1 Method

The simulation technique used are essentially those described in an earlier paper, so only a brief summary is given here. The geometry to be investigated is the azo- isomeric multilayered structure shown in Fig. 2. The laser beam's incident on the disc from the substrate side and has a wavelength of 780 nm with a Gaussian radial profile and an exp(-l) power radius of 0.4 μm. The laser was operated for a total time of 460 ms, with an interval ramp of 10 ms to full power and a shut-down ramp of 10 ms. In the evaluation of CD-R recording characteristics, the 3T signal is used as a standard writing laser pulse and corresponds to 460 ms in time. The laser heat absorbed in the layers was numerically calculated based on the works of Mansuripur et al. The spatial heat flux with unit intensity of incident light was numerically calculated, and the rate of energy absorption per unit volume of each layer was calculated. This volume heat flux is used as the input for the second model using a commercial finite element package, ANSYS. Latent heat effects were not included because it is very complicated to calculate in case of organic materials. The physical properties used in the calculation and the other properties of each layer material are shown in Table 1.

2.2 Temperature profile

Figure 3 shows the temperature variations in the z di-
Fig. 2. The geometry, boundary conditions and laser source used for the calculations.

Fig. 3. The temperature variations in the z direction at 450 m with different writing powers.

Fig. 4. TGA and DTA thermograms of the dye used.

Table 1. The physical properties used in the calculations.

<table>
<thead>
<tr>
<th>Material</th>
<th>Refractive index</th>
<th>Thermal conductivity (W/mK)</th>
<th>Specific heat (J/kgK)</th>
<th>Density (kg/m³)</th>
<th>Young's Modulus (GPa)</th>
<th>Poisson ratio</th>
<th>Thermal expansion coefficient (10⁻⁵°C⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>1.57</td>
<td>0.2</td>
<td>1200</td>
<td>1200</td>
<td>3.0</td>
<td>0.3</td>
<td>200 x 10⁻⁵</td>
</tr>
<tr>
<td>Dye</td>
<td>2.7 – 2.05i</td>
<td>0.2</td>
<td>1500</td>
<td>1500</td>
<td>2.2</td>
<td>0.3</td>
<td>66 x 10⁻⁵</td>
</tr>
<tr>
<td></td>
<td>0.18 – 0.75i</td>
<td>315</td>
<td>129</td>
<td>19300</td>
<td>106</td>
<td>0.3</td>
<td>1.42 x 10⁻⁴</td>
</tr>
<tr>
<td>Overcoat</td>
<td>1.5</td>
<td>0.2</td>
<td>1200</td>
<td>1200</td>
<td>3.0</td>
<td>0.7</td>
<td>66 x 10⁻⁵</td>
</tr>
</tbody>
</table>
Fig. 5. The temperature variations at the center of the dye layer in the radial direction at 450 nm of recording.

Fig. 6. The temperature variations at the PC/dye interface in the radial direction at 450 nm of recording.

Fig. 7. The temperature variations of each interface at 7 mW.

ures, the temperature at the center of the r axis is the highest and decreases along the r axis with the Gaussian profile of the writing laser beam. From these results, the deformations of each layer are expected to show the large deformations at the center and to decrease along the r axis. The deformation area is approximately 1 μm.

In Fig. 7, the temperature variations of each interface at 7 mW are plotted. As shown in the figure, it is expected that the melting of the dye layer, the thermal expansion of the PC substrate and the thermal decomposition of the dye layer occur in sequence and finally the recording signals are formed by the combination of the three deformations at 7 mW.

3. Experimental

To observe the deformation effects of the dye layer and the PC substrate, CD-R discs were fabricated using a flat PC substrate and an optical glass substrate, respectively, even though only a PC substrate with a pregroove is used in a real CD-R. In the case of a real CD-R, the deformation effects of the PC substrate and dye layer are mixed after writing, as expected in the engineering analysis and therefore, it is very difficult to observe the effect of each deformation separately. To separate the PC substrate and dye layer deformation effects, a glass substrate CD-R was made. A cyanine dye with a complex refractive index, 2.7 – 0.0i, was used as the material for the recording layer. Each CD-R disc has a 240 nm-thick dye layer, which is the most optimum dye layer thickness according to the results obtained from the study of thickness variation.

Writing experiments were performed on three structures using a CD-R tester (APEX, OHMT-500) under the conditions of 2–16 mW writing power with a 780 nm wavelength laser source and a 1.3 m/s writing speed. The carrier to noise ratio (CNR) was measured with the reading power of 0.7 mW. The overcoat and gold film were removed using Scotch tape and the dye layer was washed with ethanol from the PC substrate to observe the deformed area of the PC and the dye layer surfaces by AFM.

4. Results and Discussion

The reflectance spectra of a CD-R after heat treatment are shown in Fig. 8. A glass substrate CD-R was heat treated at several different temperatures for 5 min in a convection oven and its reflectance was measured by a UV spectrophotometer (Hitachi, UV Spectrophotometer 4001). As shown in the figure, the spectra of 50°C and 100°C are similar, but a drastic change in reflectance is observed from 150°C. This reflectance change implies the change of the optical property of the dye and this change can affect the optical path difference before and after recording and therefore, it can form optically recorded signals even though there may be no large thermal deformations. Considering that the dye starts to melt at approximately 133°C, the reflectance change at 150°C is mainly due to its melting. The change of the reflectance spectra increases with the increase of the heat treatment temperature. The reflectances at 780 nm af-
ter heat treatment over 200°C are below 26%, and this is enough to form the optical signals.

Figure 8 shows the AFM images of the recorded dye layer and PC substrate surfaces with the increase of writing power. A small change of the dye surface is observed from 4 mW writing power and the deformation (bump) of the PC surface is also observed from 4 mW. As expected, any deformation of the glass substrate is not observed in the glass substrate CD-R. These experimental results are well explained by the results of the engineering analysis in the previous section. From the calculation, it was determined that the temperature of the dye layer reached the melting point at 3 mW and the temperature of the PC substrate reached Tg between 3 mW and 1 mW. For the Tg of the PC, 10°C is attained around 3.5 mW, which is a little bit lower writing power than that of the experimentally observed formation of the bump, 4 mW. In Figs. 10 and 11, the AFM analysis results of the recorded dye layer and PC surfaces are shown. Neither a bump nor a pit is formed at 3 mW, but both deformations are observed from 4 mW. The degree of deformation increases as the writing power increases. The bump height on the PC surface (Fig. 10) is 42 nm at 7 mW and the pit depth on the dye layer surface (Fig. 11) is 35 nm at 7 mW.

In Fig. 12, CNR variations of the CD-Rs with a glass and with a PC substrate were plotted. CNR is defined as the carrier to noise ratio of the written data with the same length for the recorded and unrecorded areas at the appropriate frequency, which is measured by a spectrum analyzer. CNR is one of the most important recording characteristics of optical recording media and it must be more than 47 dB to satisfy CD-R standards. In this experiment, the data was recorded at a 720 kHz frequency. In the figure, CNR has the first threshold at 3 mW and increases rapidly to 3.5–4.0 mW in both CD-Rs. From this writing power, the two CD-Rs show different recording characteristics. A glass substrate CD-R has a stagnancy between 4 mW and 6 mW, and shows the second threshold at 6 mW. On the other hand, a
PC substrate CD-R shows a very short stagnancy between 3.5 mW and 4 mW and the CNR increases again to 6 mW and shows an almost saturated value at 7 mW. However, in the high writing power range over 9 mW, it decreases. As shown in the figure, the temperature of the dye layer center reaches its melting point at 3 mW, which is a driving force of the increase of CNR by approximately 4 mW in both CD-Rs. On the other hand, a glass substrate CD-R has no CNR increase between 4 mW and 6 mW because there is no more additional deformation of the dye layer or of the glass substrate prior to the thermal deformation of the dye. Although the dye layer decomposition temperature is attained at 5 mW from the calculation, the second threshold is observed around 6 mW. This might be because the laser beam recording is conducted instantaneously with timescales of 10^{-10}^s and this high heating rates are capable of significantly elevating the dye decomposition temperature. We believe that these high heating rates result in the delay of the second threshold of CNR. On the other hand, a PC substrate CD-R shows a short stagnancy of CNR at 3.5-4.0 mW, and the CNR increases again at 4.5 mW. This is quite different from the glass CD-R, and it is considered that this difference is due to the PC deformation effects. CNR did not increase immediately even though a bump is observed at 4 mW from the AFM image because the bump formed in low writing power range cannot significantly contribute to CNR due to its small size. Compared with a glass substrate CD-R, a PC substrate CD-R has a wide range of optimum CNR from 6 mW to 10 mW. Furthermore, its optimum starts from a much lower writing power of 6 mW than that of the glass substrate CD-R. This is very important in fact that a CD-R must have more than 60% reflectivity to satisfy CD-R standards. Most of the writing laser beam is reflected and only a limited quantity of the laser beam, normally below 25%, can be used for heat generation. Most dyes for optical recording media have decomposition temperatures higher than 200°C, and do not decompose easily in a low writing power range. Because a CD-R must have a CNR of more than 45 dB between 4 mW and 8 mW, the PC substrate plays an important role, not only as a substrate, but also as one of the signal forming parts in the low writing power range. The PC substrate has been considered to be a simple substrate, but its thermal deformation should be carefully considered to obtain satisfactory specifications of a CD-R. In the high writing power range over 9 mW, the decrease of CNR is observed, even though the writing power increases. This can be explained by the excessive deformation of the PC and dye layer in the high writing power range. The decrease of CNR in the PC substrate CD-R is larger than in the glass substrate CD-R because the excessive deformations of the dye layer and PC occur simultaneously and the combined deformations result in negative effects on the CNR.

5. Conclusions
The temperature variations of the layers in a CD-R were numerically calculated and predicted the deformation of the dye layer and the PC substrate well. The thermal deformations of the dye were observed successfully with a glass substrate CD-R by AFM analysis, and those of the PC were observed with a flat PC substrate CD-R. Each thermal deformation effect was interpreted by the recording characteristics, the CNR. From the trends of CNR it is clearly understood how the deformation of the dye layer and the PC affect the CNR. A PC substrate CD-R shows a better CNR in the writing power range.
of 4.0–6.0 mW, the deformation of the PC substrate contributes to the CNR increase and the PC plays an important role to efficiently improve the CNR in this low power range. The PC substrate has been considered as a simple substrate which supports the dye recording layer, but its thermal deformation should be carefully considered to obtain satisfactory specifications of a CD-R.