Effects of Bi on crystallisation in Ge–Sb–Te–Bi

S. F. Chen, J. K. Chen* and T. P. Chen

Blue light optical storage products will become the next generation devices for recording media in the near future. To increase the crystallisation speed of recording by 405 nm wavelength blue laser diode, bismuth (Bi) is applied to substitute small quantities of antimony (Sb) in a pseudobinary GeTe–Sb2Te3 (GeSb2Te4) alloy material. It is shown that the activation energies for crystallisation of Ge–Sb–Te–Bi are reduced by addition of Bi indicating the improvement of recording speed. The Ge–Sb–Te–Bi material is incorporated into actual blue light phase change optical disks and is found to provide good land and groove recording characteristics, cross-talk characteristics, and cross-erase characteristics. It is demonstrated a promising candidate for HD DVD-RAM applications.

Keywords: Crystallisation speed, Blue light optical disk, Optical recording, Phase change media

Introduction

Selections of recording materials for blue light optical rewritable disks are very important in developing next generation storage media. Ever since the chalcogenide phase change materials were first applied for memory devices in 1968,1 it has been a constant effort to improve recording speed of these materials with increasing recording density. Yamada et al.2,3 show that the recording speed of Ge–Sb–Te systems is ideal for phase change optical disks. Such systems have shown its wide applications in CD-RAMs and DVD-RAMs.

To modify Ge–Sb–Te system suitable for applications in blue light optical rewritable disks, the crystallisation speed must be improved. The low melting point and large atomic size make bismuth a possible choice to accelerate the crystallisation of current Ge–Sb–Te system.4 In the present study, two different levels of bismuth concentrations were added to substitute antimony content in the GeTe–Sb2Te3 tie line to achieve higher crystallisation speed. Crystallisation behaviours of these new materials for applications in blue light optical disks are discussed. The recording properties of optical disks utilising this material are also reported.

Experimental

Two different compositions of phase change sputtering targets were made through vacuum melting and hot pressing. Bi content of 2 and 4 at.% was added to a GeSb2Te3 composition selected in the GeTe–Sb2Te3 tie line. These materials of 100 nm were deposited on 0.6 mm polycarbonate substrates separately using Shibaura Speed 12. These deposited films were then crystallised using an 800 mW laser power. Low angle X-ray diffraction (XRD) spectra of these crystallised phase change film were obtained using Cu Kα characteristic wavelength to examine the crystal structures of the phase change films.

Powders of the as deposited phase change materials were scratched from the sputtered film to perform differential scanning calorimetry (DSC) experiments at heating rate ranging from 5 to 20 K min⁻¹. The activation energy of crystallisation was then evaluated by Kissinger’s plot

\[
\ln \frac{x}{T_x^2} = \frac{E_a}{k_B} \times \frac{1}{T_x}
\]

where \(x\) is heating rate (K min⁻¹), \(T_x\) the phase change temperature in Kelvin, \(E_a\) the activation energy for crystallisation and \(k_B\) Boltzmann constant.

To simulate HD DVD-RAM configurations, the stack structure of Ag–ZnS–SiO2–GeSbTeBi–ZnS–SiO2 thin films (Fig. 1) was sputtered on 0.6 mm polycarbonate substrates and glued with another 0.6 mm dummy polycarbonate substrates. A Pulstec ODU-1000 tester using 405 nm wavelength blue laser and object lens with the NA of 0.65 was employed to characterise record and erase the performance of these optical disks. The

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1 Cross-section structure of blue light rewritable optical disk

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optimised writing power can then be obtained from modulations of disk partial respond signal noise ratio (PRSNR) and lower signal bit error rate (SBER) with writing power.5

Transmission electron microscope samples were prepared from the disk sample by separating the disks into two 0.6 mm polycarbonate stacks. One of them contains dummy polycarbonate substrate and the reflective layer. The other consists of polycarbonate substrates and the dielectric and phase change films. The polycarbonate substrates containing phase change films were then dissolved by tetrahydrofuran solvent.6 Carbon coated copper grids were then used to collect the residual thin films for TEM observations.

Ge–Sb–Te–Bi material with 70 nm films containing 2% and 4%Bi was also sputtered on top of carbon coated copper grids for TEM observations. The TEM observations were all performed on a JEOL 2100F operated at 200 keV. Scanning electron microscopy was performed on a Hitachi S-4700 to observe the written data on the disks.

Results and discussion

Crystal structure of Ge–Sb–Te–Bi

Low angle X-ray diffraction results of crystallised (GeSb2Te4)0.98Bi0.02 and (GeSb2Te4)0.96Bi0.04 films are shown in Fig. 2. The spectra show only a few diffused peaks due to the low thickness of films. The d-spacing of these peaks in two compositions is fairly close with each other. These peaks were analysed to be consistent with NaCl crystal structure as reported in Ref. 7.

Furthermore, the XRD spectra of (GeSb2Te4)0.98Bi0.02 and (GeSb2Te4)0.96Bi0.04 films were numerically analysed using least square method to obtain the lattice parameter in each composition. The lattice parameters of 2% and 4%Bi were analysed to be 5.959 and 5.965 A, respectively. The increased Bi concentrations appear to affect little on the lattice parameters. These results are complementary and in good agreement with a separate study by Yusu.8 Since the atomic size of bismuth is much greater than other elements in Ge–Sb–Te, it is expected the lattice parameter of 4%Bi composition larger than 2%Bi composition. The substitutions of smaller Sb atoms with larger Bi atoms can lead to increased vacancy concentration. Such modification in the crystal structure can increase atomic mobility and thus give rise to a higher crystal growth rate.

Activation energy of crystallisation by DSC analysis

Figure 3 shows the Kissinger plots of ln (α/T²) versus 1/T. The slope obtained by linear regression gives the corresponding activation energy. Ge–Sb–Te with an addition of 2% and 4%Bi has 2.55 and 2.52 eV respectively. The crystallisation temperatures range from 432 to 441 K depending on the heating rate. The crystallisation temperatures of 4%Bi added composition are constantly lower than that of 2%Bi films at all heating rates.

These values of activation energy and crystallisation temperatures appear to be higher than the data of Ge–Te–Sb2Te3 systems reported earlier by Yamada et al.9 The difference might be due to partial oxidation of the powder samples for DSC studies which increase the barrier for crystallisation.

From the activation energies obtained in the present study, the addition of Bi apparently decreases the activation energy slightly. The lower activation energy reduces the threshold for crystallisation. Bi addition therefore increases the crystallisation speed. This can be explained by the larger bismuth atom expanding the lattice structure such that they reduce the structural difference between amorphous and crystalline phases as proposed in Ref. 4.

Transmission electron microscope observations of deposited films

The as deposited films of both 2% and 4%Bi added phase change layers are both amorphous as shown in Fig. 4a. The as deposited films were then exposed to converged 200 kV electron beam for TEM observations. After exposure, Fig. 4b shows that films of both compositions start to form crystallites with cube symmetry. This phenomenon is consistent with observations reported elsewhere in other material system.9 The crystallisation of films was also observed to increase qualitatively with the duration of electron beam exposure.

The actual blue light disk films containing phase change layers and track structures were also observed via both SEM and TEM. Figure 5 shows the well defined written areas as clear recording marks indicating good signal recording.

Disk performance

The ODU-1000 measurements (Table 1) indicate that both the 2% and 4%Bi disks perform very good characteristics in overwriting ability. Figure 6 shows
The optimised writing power is \( \sim 6 \, \text{mW} \) which conforms to the specifications of HD DVD-RAM disks. The two compositions of phase change layers can both fulfil the specification requirements.

Furthermore, the 4\%Bi disks demonstrate characteristically higher PRSNR and lower SBER than 2\%Bi disks except the single track PRSNR value (Table 1). The improvement of five track overwriting performance in the 4\%Bi disks suggests that the 4\%Bi added phase change layer causes less cross-talking problems, thus maintaining better signals after multiple track writing. This may be in part explained by more stable crystal structures and slightly higher heat capacity in the higher bismuth added composition.

**Conclusions**

The crystallisation speed of 2\% and 4\%Bi phase change material has been shown to meet the requirements of blue laser rewritable media. HD DVD-RAM disks are made using either compositions as their phase change materials. The substitution of bismuth for antimony in Ge–Sb–Te appears to increase the crystallisation speed. The XRD results confirm that the Ge–Sb–Te–Bi crystallites bear a NaCl structure. The lattice parameters of these crystallites increase with the concentration of Bi. The larger atomic size and lower melting point of Bi are responsible for lowering the temperature and activation energy of crystallisation, thus increasing crystallisation speed.

<table>
<thead>
<tr>
<th>Material</th>
<th>2 at.-%Bi</th>
<th>4 at.-%Bi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameter, ( \text{Å} )</td>
<td>5.959</td>
<td>5.965</td>
</tr>
<tr>
<td>Crystal structure</td>
<td>NaCl</td>
<td>NaCl</td>
</tr>
<tr>
<td>Activation energy, eV</td>
<td>2.55</td>
<td>2.52</td>
</tr>
<tr>
<td>PRSNR Land</td>
<td>1 Track 10 times: 21.7</td>
<td>20.2</td>
</tr>
<tr>
<td></td>
<td>5 Track 10 times: 15.7</td>
<td>17.4</td>
</tr>
<tr>
<td>Groove</td>
<td>1 Track 10 times: 22.5</td>
<td>23.9</td>
</tr>
<tr>
<td></td>
<td>5 Track 10 times: 15.9</td>
<td>17.8</td>
</tr>
<tr>
<td>SBER Land</td>
<td>1 Track 10 times: 5.2e-6</td>
<td>2.1e-6</td>
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<tr>
<td></td>
<td>5 Track 10 times: 1.8e-5</td>
<td>4.4e-6</td>
</tr>
<tr>
<td>Groove</td>
<td>1 Track 10 times: 4.2e-6</td>
<td>1.7e-6</td>
</tr>
<tr>
<td></td>
<td>5 Track 10 times: 1.6e-5</td>
<td>7.5e-6</td>
</tr>
</tbody>
</table>

**Table 1** Disk performance of Ge–Sb–Te–Bi phase change materials with 2\% and 4\%Bi additions.
Acknowledgements

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References