

Comparison of Te-rich and Sb-rich Phase-Change Materials
on Overwrite Characteristics
and on Limitation in Number of Recording Layers

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Abstract

Overwrite characteristics are compared for Te-rich and Sb-rich phase change materials. Merits and Demerits of these materials are clarified using a model taking differences between covalent bond and ionic bond into consideration. Limitation in number of recording layers, double or triple, has also been investigated for Te-rich and Sb-rich phase-change materials introducing a new process having small spacer-layer thickness deviation.

Introduction

Phase-change optical disk has many merits. Those are one-beam overwrite, read-out by reflectivity difference, possibility of double layer disk, etc. However, these properties strongly depend on material characteristics, and to control amorphous material characteristics is difficult. Usually, phase-change is treated by JMA (Johnson Mehr Avrami) equation, but discrepancy between the theory and experiment often appears because JMA equation is a macroscopic equation. In this paper, we try to explain dependence of phase-change disk characteristics on recording film material introducing difference between covalent bond and ionic bond.

Experiment

Two major compositions of Phase change recording material are Te rich composition, for example, $\text{Ge}_2\text{Sb}_2\text{Te}_5$, and Sb rich composition, for example, $\text{Ag}_4\text{In}_8\text{Sb}_{65}\text{Te}_{23}$. Comparison of Te rich and Sb rich composition has been carried out experimentally.

In the case of Te rich composition, several compound compositions, for example $\text{Ge}_2\text{Sb}_2\text{Te}_5$, exist. Compound-composition recording material is advantageous for fast crystallization because only one kind of crystal is formed and long-range atom diffusion to form more than two kinds of crystals from homogeneous amorphous state is not necessary. Although bulk Te has hexagonal crystal structure, we proposed a NaCl-type crystal structure model ¹⁾ as shown in Fig.1, because result of the structure analysis by electron beam diffraction in TEM showed that the crystal structure of the Te rich film (Ag-Ge-Sb-Te) was NaCl-type. This structure-model was confirmed by EXAFS analysis etc. later ²⁾. So, metallic element site and Te site are the same in number. However, Ag added $\text{Ge}_2\text{Sb}_2\text{Te}_5$ contains about 55 at% Te, so, about 10% of (Ag,Ge,Sb) site is vacant. When the recording film becomes amorphous, vacancies are partly collapsed, so, amorphous state can have higher density than the crystalline state although this is extraordinary. Crystallization of Te-rich recording material occurs by crystal nucleation then growth.

Sb-rich recording material has fast crystal-growth speed, but very slow crystal nucleation speed. The crystal growth speed depends on the Sb content of the recording film. Excess Sb speeds up the growth speed, and Sb content can be as large as 85 at%. However, too much Sb content decreases durability against read laser beam. These phenomena seem to be caused by fast Sb crystal growth

overwhelming other constituent elements.

Discussion

1. Effect of ionic bonds on crystallization speed

Nucleation and growth rate is related to crystal structure, and crystallization activation energy is also related to crystal structure. We propose a crystallization model that takes difference of covalent bond and ionic bond into consideration. Crystallization mechanism is very complicated, however simple model will be able to explain most of crystallization features. Ionic bond makes crystal nucleation easier than covalent bond because ionic bond is more flexible than covalent bond. An example of changeable ionic bond between a metal and a chalcogenide element ³⁾ is shown in Fig.2 ³⁾. The change from (a) to (b) can be an effective trigger of crystal nucleation. The situation will be the same even when Se is replaced by Te because oxygen, sulfur, selenium and tellurium belong to the same group in the periodic table. However, long-range atomic rearrangement is more difficult in the case of ionic bond in low temperature range because Coulomb force is a longer-range force. The faster nucleation and slower crystal growth in low temperature range caused by above mentioned characteristic of ionic bond is desirable for Te-rich recording film. And ionic bond makes crystallization activation energy larger as shown by a dotted curve in Fig.3 because crystal growth speed greatly depends on temperature due to ionic bond's multi-energy-barrier interaction between atoms. Dependence of softening temperature of SiO₂ glass on ionic oxides (K₂O and TiO₂) contents ⁴⁾ is shown in Fig.4. Here we use data of amorphous oxides because in the case of chalcogenide recording material, measurement of glass-transition temperature that is related to starting temperature of crystal nucleation is quite difficult because the material crystallizes very fast. Softening (glass transition) temperature goes up along with TiO₂ content increase, although it goes down by too much TiO₂ addition. This shows that introduction of ionic bond increases stability of amorphous state in low temperature range without decreasing crystallization speed (judging from viscosity data not shown in the figure) in high temperature range. This stabilization of amorphous state is partly caused by the fact that metallic plus ion has small diameter and decreases spaces between minus-ions forming basic structure in low temperature range. This is very good characteristics to obtain large stability of amorphous state, that is, long storage life and high durability against read laser beam. However, too much addition of ionic compound

decreases amorphous-state stability because many plus-ions become to move to interstitial or charged defect positions. Electronic negativities of elements ⁵⁾ are shown in Fig. 5. Elements whose position in the figure are far from Te has a tendency to form ionic bonds. Addition of Sn ⁶⁾ or Bi ⁷⁾ is reported to make crystallization faster. These elements are considered to make chemical bonds having more ionic characteristics.

The crystallization speed-up effect of up to 20% In addition to Sb-rich recording material ⁸⁾ is also considered to be caused by ionic tendency of the chemical bonds between In and other elements.

2. Dependence of refractive index on wavelength

The optical characteristics of Sb-rich recording material are much different from Te-rich recording material at the wavelength of 660nm, but it is similar to Te-rich recording material at the wavelength of 400nm. However, remaining small difference has some influence on possibility of multi-layer recording. Refractive index of the material depends on material density and electronic states. An example where refractive index of amorphous material depends on its density is shown in Fig.6 ⁹⁾. In ordinary material, refractive index is larger in crystalline state because crystalline state has higher density. However, if density of crystalline state is lower than that of amorphous state due to above-mentioned vacancy, to have lower refractive index is not strange.

The refractive index curve crosses at a wavelength of about 650nm as shown in Fig. 7. This is explained by above-mentioned model. The fact that refractive index value of crystalline state at shorter wavelength range than 660nm is lower than that of amorphous state is explained by the vacancy model. At longer wavelength than 660nm, electron-photon interaction increases because the photon energy approaches band-edge energy and absorption increases. This is considered to be the mechanism of rapid extinction coefficient and refractive index increase towards long-wavelength side in crystalline state. In the case of amorphous state, refractive index change is small because density of states change towards long-wavelength side around the band edge is gradual. This is considered to be the mechanism of curve crossing.

3. Effect of ionic bond on the double layer disk

Introduction of ionic bond is also desirable in obtaining suitable recording film characteristics for double layer phase-change disk in terms of high optical

transmittance. Because ionic bond that is bonding with long distance elements in the periodic table, makes optical band gap larger and increases transmittance of visible light. Large transmittance can also be achieved by decreasing film thickness, but crystal nucleation speed quickly decreases in this case because vibration of recording-film atoms that generates crystal nuclei becomes suppressed by adhesive force to protective layers. In the case of introduction of ionic bonds, crystal nucleation speed increases as mentioned above, so the situation is better.

When comparing Te-rich recording material and Sb-rich recording material, Sb rich recording material need not worry about crystal nucleation speed decrease by decreasing recording film thickness because crystallization is mostly by crystal growth. However long range crystallization without stopping by irregularity in substrate surface is necessary. So, minimum thickness of recording film can not be so thin. And further, the fact that recording material is constituted mostly by Sb restricts variation of optical characteristics. Therefore, Te rich recording material is a little advantageous in designing double layer phase-change optical disk.

4. Desirable spacer layer formation process for double layer disks

In order to decrease the heavy load to recording film in designing a double layer disk, we developed a new spacer layer forming technique to form a uniform-thickness spacer layer by using a 20 μ m-thick sheet of organic resin ¹⁰. This sheet has rapidly changeable surface hardness. Initially, sheet surface is soft and sticky, and after UV light irradiation, the polymerization reaction becomes ready to start. By passing through heated rollers, only the surface of the sheet is quickly heated and softened and becomes easy to replicate the stumper surface pattern. Shortly after that, the polymerization reaction starts, and surface hardness quickly increases, so the stumper can be separated from the sheet without any damages on the replicated pattern. It is better to carry out after-heating in order to increase hardness up to a level enough to endure the high temperature during the recording. The thickness variation of the spacer layer all over the disk was plus minus 1 μ m.

Conclusion

Crystallization and optical characteristics of phase-change recording films is investigated by using a model taking differences between covalent bond and ionic bond into consideration. Adaptability of recording material to double layer phase change disk is also examined based on this model. Crystal nucleation mechanism due to ionic bonding transition is expected. A new method to make a spacer layer having very accurate thickness between two recording layers has also been introduced.

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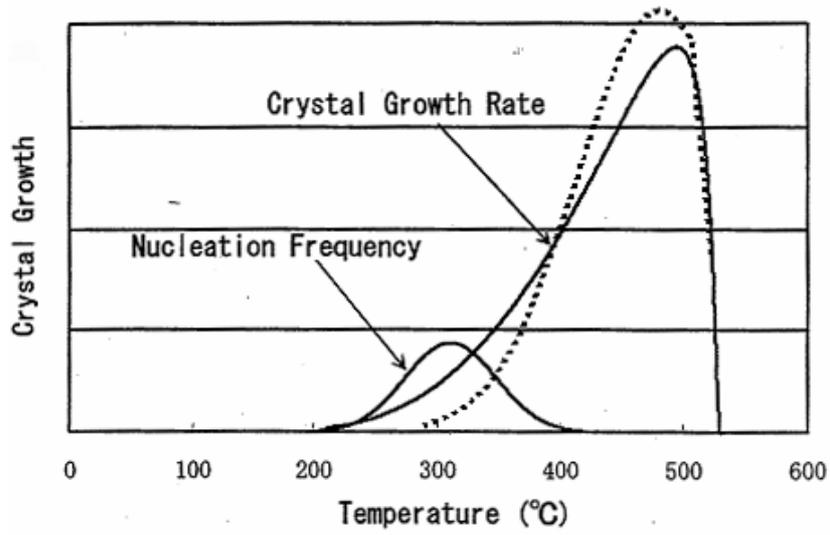


Fig. 3 Crystal nucleation rate and Growth rate of Te-rich material

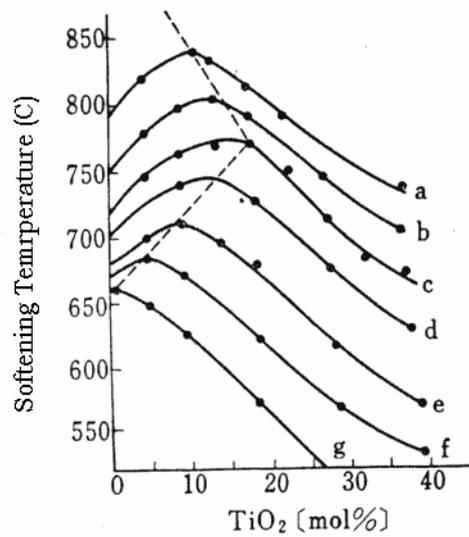


Fig. 4 Change of softening temperature
K₂O content increases from a to g.

Fig. 5 Electronegativity of elements

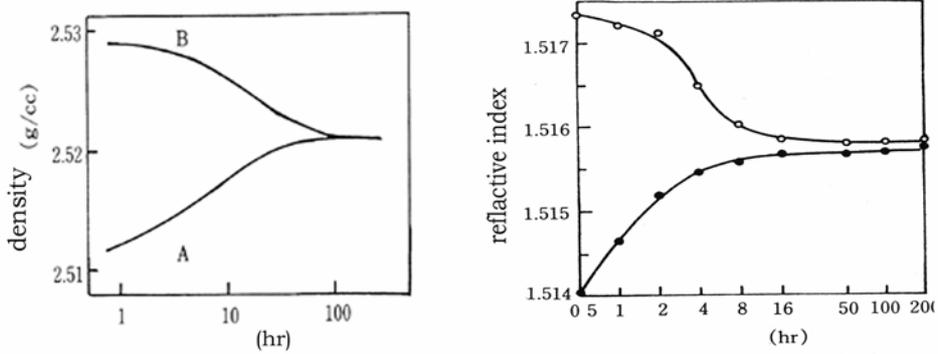
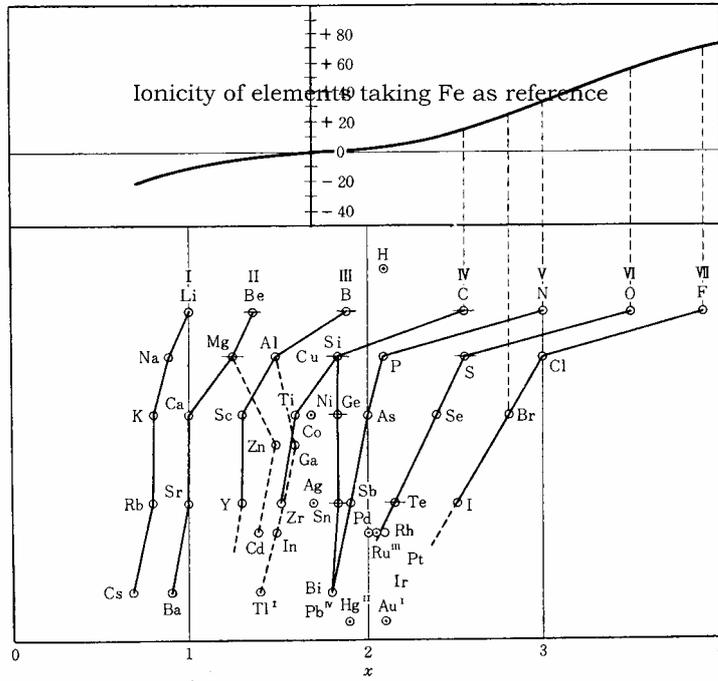


Fig. 6 Refractive index change accompanying density change during annealing at 520 C for boron silicate glass. A: Quenched from 600 C B: 490 C 6 weeks

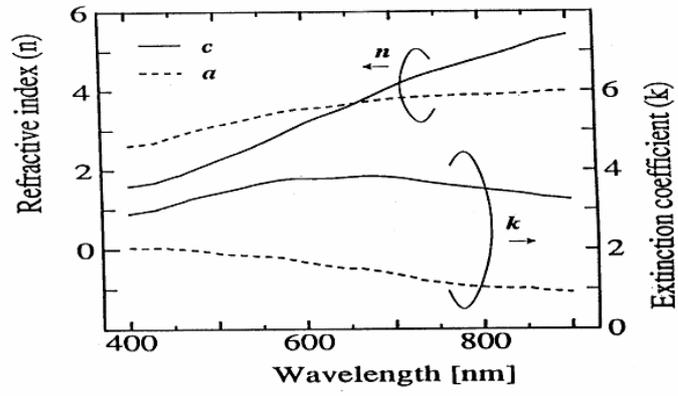


Fig. 7 n and k value vs wavelength