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X-ray Diffraction Analysis of Ag-In-Sb-Te Thin Films

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The x-ray diffraction experiments were carried out to investigate the phase transfomation of the sputter-deposited Ag-In-Sb-Te optical thin films after rapid thermal annealing and while being annealed with high-temperature x-ray attachment. The formation mechanism of the reported mixed phase, with both amorphous phase and fine crystalline AgSbTe2 phase, of Ag-In-Sb-Te system in its ordered state was explained. Moreover the characteristics of the other phases which appear during the annealing processes were also discussed in the present article.

I. INTRODUCTION

Phase change optical disc has attracted great research interest since it is one of the most promising candidates for rewritable storage for multimedia. As a result, phase change optical recording technology has been developed rapidly over the past few years and a great variety of phase change optical recording materials have been extensively investigated ever since. Among the recording materials, Ge-Sb-Te intermetallic compound systems have been widely investigated. However, this recording material has big absorption difference between ordered (crystal) state and disordered (amorphous) state making it difficult to adopt mark edge recording format. Mark edge recording format is one of the state of the art technology finding its way to be applied to phase change optical disk, which require precise control of the mark length and edge shape. Recently, attempts to make phase change optical disk compatible with compact disk read only memory (CD-ROM) have been made by Philips and Ricoh.This approach is based on the use of mark edge recording just like CD-ROM. In fact, two approaches are possible to resolve the absorption difference problem; absorption control by disk structure redesign (reverse absorptivity) and new alloy design such as Ag-In-Sb-Te system. The most unique characteristics of Ag-In-Sb-Te system compared to Ge-Sb-Te system is that there exists mixture of amorphous phase and crystal phase at the same time in its ordered state[1]. It has been known from the earlier study that the co-existence of crystal and amorphous phases reduces the absorption difference and the amorphous phase prohibits the grain growth of crystal phase to form fine crystallites. However, phase transformation in this alloy system occurs in complex manner because of its mixed phased involved. Therefore, the main purpose of this research is to clarify the phase change process of sputter-deposited Ag-In-Sb-Te films by the combined use of rapid thermal process (RTP) unit and high-temperature X-ray attachment. We tried to explain the co-existence mechanism of $AgSbTe_2$ crystal phase and amorphous phase of remnant In and Sb in the ordered state. Moreover characteristics of the other phases which appear during the annealing processes were also discussed in the present article.

II. EXPERIMENT

A Ag-In-Sb-Te alloy was deposited on silicon substrate by dc-magnetron sputtering from sintered Ag-In-Sb-Te target. Thickness of the deposited film was about 1000 Å determined by grazing angle X-ray reflection method using D^3 system of Bede Scientific Incorporate. The chemical composition of the deposited film was analyzed by using ICP-AES (Inductively Coupled Plasma/Atomic Emission Spectrometer). Crystallization temperature and melting point of sputter-deposited film was measured by means of differential scanning calorimetry(DSC). The heating rate was 10°C/min. We simulated crystallographic structure of important phases such as Sb and $AgInTe_2$ and $AgSbTe_2$ with Powder Cell and x-ray diffraction patterns of them with Rietveld[2]. The structures of the Ag-In-Sb-Te target and sputter-deposited films were analyzed by means of X-ray diffractometry (XRD). The X-ray source was Cu with a wavelength 1.5406 Å. We used $2\theta-\theta$ axis and wide angle goniometer while getting the diffraction spectra from the bulk target and high-temperature XRD and we used θ axis and thin film attachment using incidence angle of 3° while getting the XRD pattern of the RTP annealed film. Heat treatments for the study of phase transformation were carried out by using two appratus; (1) We used high temperature attachment of X-ray diffraction system heating the film from room temperature to 500°C. The heating rate was 5 degrees/min and the holding time was 30min for each temperature. (2) We used RTP unit annealing the film at various temperatures from 150°C to 700°C and then got the XRD patterns of each annealed samples. The schematic diagram of RTP experiment procedure is shown in figure 1. The annealing time was fixed at 1 min at each temperature and annealing was carried out while flowing N_2 gas. The real temperature of the film was detected with a thermocouple and turned out to follow well the programmed temperature. During the cooling process after heat treatment, the temperature dropped 70~150 degrees instantly, depending on the annealing temperature, because of the purging N_2 gas and then the sample cooled slowly afterward.

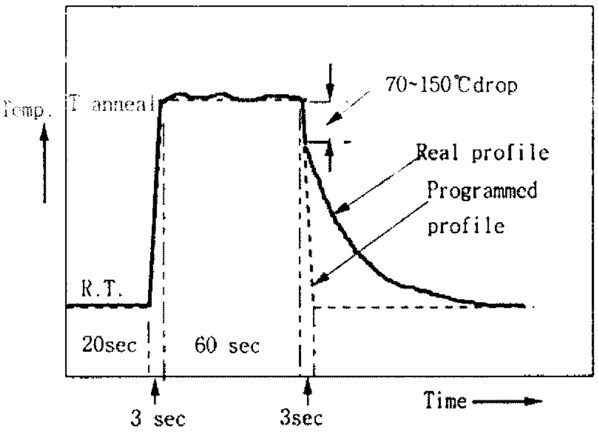

Figure 1. The schematic diagram of RTP procedure. The annealing time was fixed at 1 min for each annealing temperature.

III. RESULTS

The DSC curve obtained for the as-deposited single-layered Ag-In-Sb-Te film is shown in Fig.2. The atmosphere during heating was N_2. An exothermic peak is observed approximately at 184.5°C. Therefore the amorphous to crystal phase transformation occurs at 184.5°C in Ag-In-Sb-Te film. The melting point is around 420°C. The peak is broad because the film consists of multi-phase.

The chemical compositon of the deposited thin films determined by ICP-AES is Ag5/In7/Sb61/Te27 in atomic percent.

Figure 3 shows the crystal structures of (a) Sb and (b) $AgInTe_2$ and (c)$AgSbTe_2$. Sb is a rhombohedral structure with $R_{-3\ 2/m}$ space group. $AgInTe_2$ is a tetragonal structure with $I_{4\ 2\ d}$ space group, which is so called chalcopyrite structure[3]. $AgSbTe_2$ is a cubic structure with $F_{4/m\ -3\ 2/m}$ space group.

Figure 4 shows the XRD patterns of the above three phases. It is simulated with Rietan[2] program for structure refinement. They give many other information such as unit cell volume, ideal density, distance between atoms, angles between atoms, etc. Figure 5 shows the XRD patterns of the Ag-In-Sb-Te bulk target. The diffraction peaks are assigned as a mixture of $AgInTe_2$ with the chalcopyrite structure and the elemental Sb.

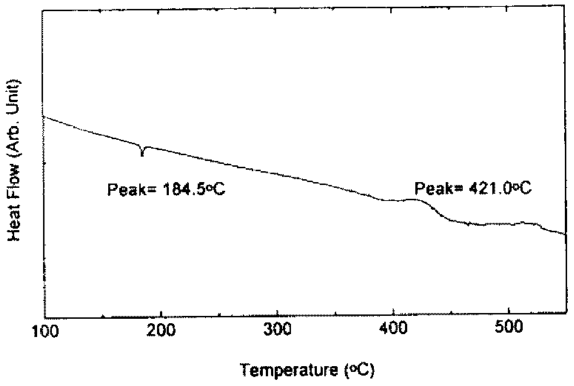

Figure 2. The DSC curve obtained for the Ag-In-Sb-Te film in the N_2 atmosphere.

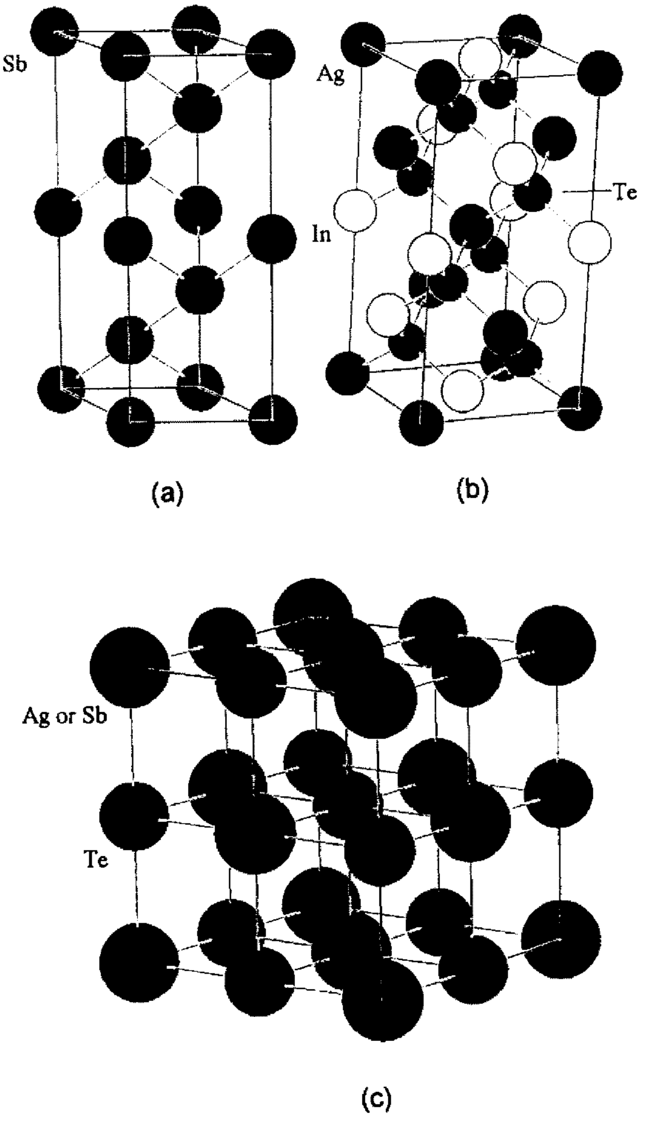

Figure 3. Crystal structures of (a) Sb $R_{-3\,2/m}$(b) $AgInTe_2$ $I_{-4\,2\,d}$ (c) $AgSbTe_2$ $F_{4/m\,-3\,2/m}$ simulated with Powder Cell.

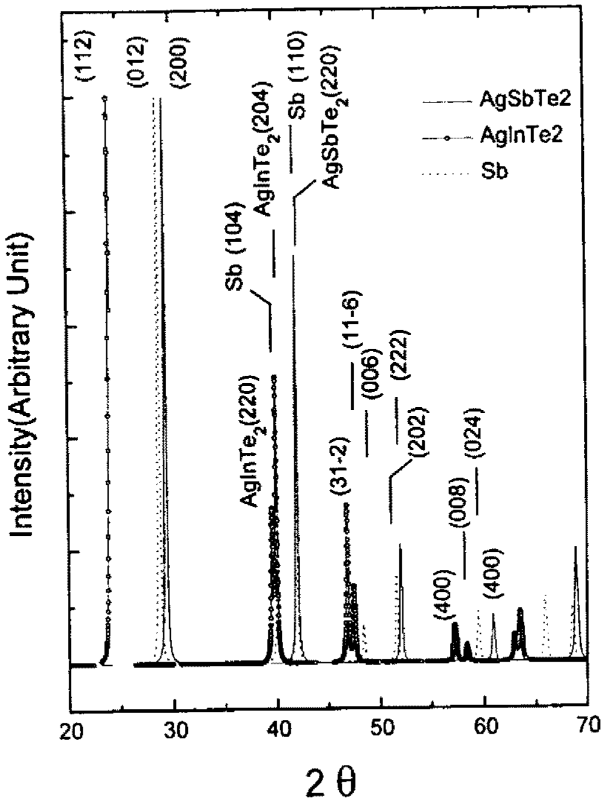

Figure 4. Simulated XRD patterns of AgInTe2 and Sb and AgSbTe2 based on the structures shown in figure 3.

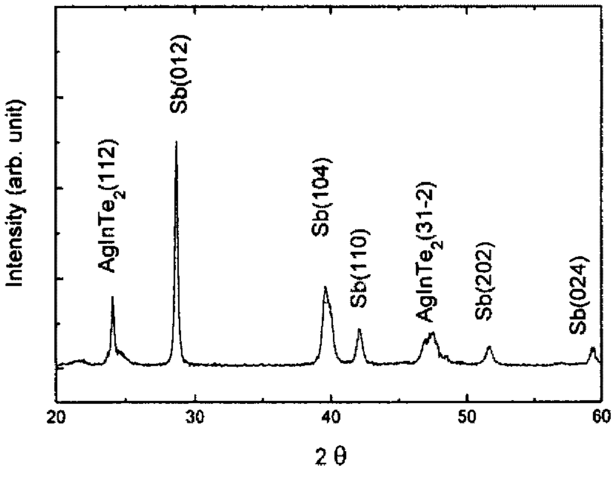

Figure 5. XRD patterns of the Ag-In-Sb-Te bulk target. Analyzed as a mixture of $AgInTe_2$ and Sb

Figure 6 shows the high-temperature XRD patterns of the Ag-In-Sb-Te film. In pattern (a), no peak is observed and therefore the as-deposited film was in an amorphous state. Pattern (d) shows two peaks which is assigned to Sb phase, indicating that the crystallization occured between 140°C and 160°C. In pattern (d) the peaks are small and broad and up to 300°C they grow bigger and sharper. It means as temperature ascended the crystalline grains became bigger. Small $AgInTe_2$ peak appeared in pattern (g) can be interpreted as $AgInTe_2$ phase is formed at higher temperature than Sb phase and that its portion is smaller than that of Sb phase. In phase (i) all peaks disappeared, so we can conclude that Sb phase of Ag-In-Sb-Te thin film melted between 400°C and 500°C which is much lower temperature than the melting temperature of pure bulk Sb which is 630.74°C.

Figure 7 shows the XRD patterns of the Ag-In-Sb-Te film (a) as-deposited, (b) ~ (k) after annealing at 150°C ~ 700°C for each pattern in thin film mode. In pattern (a), very broad peaks are observed but we can say that as-deposited film is an amorphous phase. In pattern (c), sharp peaks start to appear, so the amorphous phase has changed to crystalline phase of Sb and $AgInTe_2$. From pattern (c) to pattern (g), the $AgInTe_2$ and Sb peaks get sharper and bigger which means that as temperature ascends amorphous to crystalline phase change increases and that crystalline grains grow bigger. In pattern (h), different phase $AgSbTe_2$ appears. According to the DSC result the melting point of Ag-In-Sb-Te film is considered to be between 4420°C. Therefore we concluded that around 450°C the Ag-In-Te-Sb thin film melts and because of the RTP characteristics, the temperature drops very quickly approximately 70~150°C bringing about quenching effect right after the annealing, consequently producing high temperature phase $AgSbTe_2$.[4] At higher temperature above 450°C, in patterns (i) and (j) and (k), another phase appears which we haven't analyzed yet. It is considered to be because of the longer annealing time during which other phase forms. So the phase transformation from liquid to $AgSbTe_2$ takes place in very short time compared to other phases. This result coincides with the earlier work reporting that the phase transformation from amorphous to $AgSbTe_2$ in Ag-In-Sb-Te thin film occurs within hundreds of nanoseconds.[5]

IV. CONCLUSION

Several phases that appear while annealing Ag-In-Sb-Te film with high-temperature x-ray unit and RTP were analyzed with x-ray diffraction method. The as-deposited film was amorphous while the transition

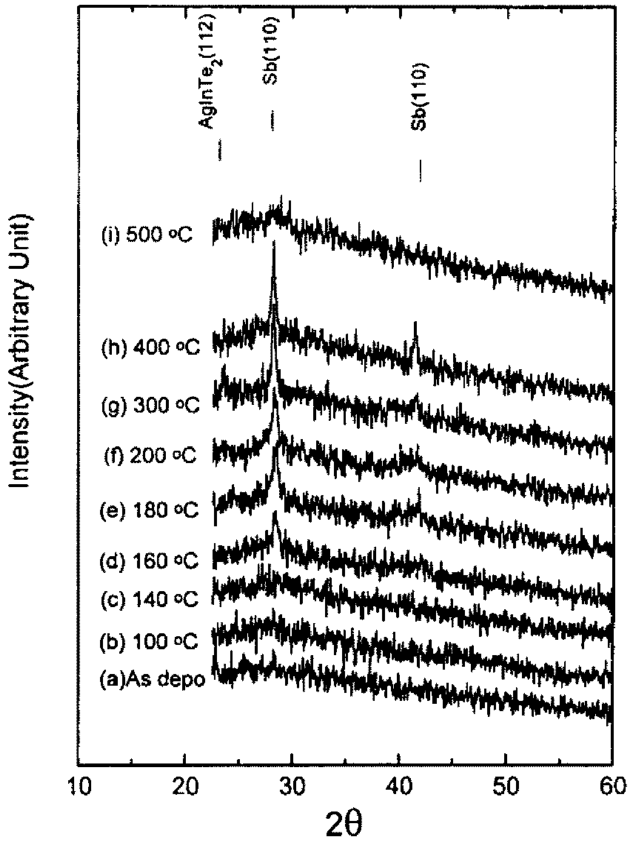

Figure 6. The high-temperature XRD patterns of the AG-In-Sb-Te film (a)as-deposited (b)at 100°C (c)at 140°C (d)at 160°C (e)at 180°C (f)at 200°C (g)at 300°C (h)at 400°C (i)at 500°C

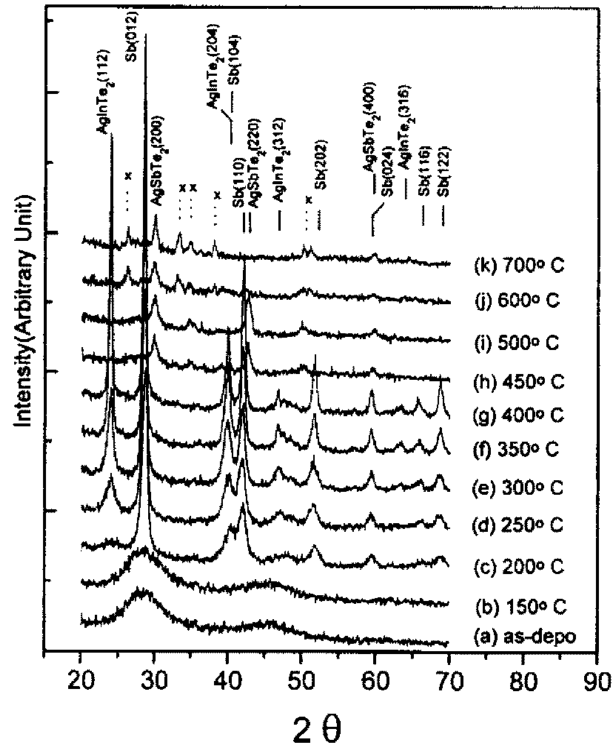

Figure 7. The XRD patterns of RTP annealed AG-In-Sb-Te film (a)as-deposited (b)at 150°C (c)at 200°C (d)at 250°C (e)at 300°C (f)at 350°C (g)at 400°C (h)at 450°C (i)at 500°C (j)at 600°C (k)at 700°C

temperature from as-deposited amorphous to crystalline phase was 184°C according to DSC result. The melting point of mixture of $AgInTe_2$ and Sb phase was found to be 420°C according to DSC and confirmed by high-temperature XRD result.

In rapid thermal processing experiment, the $AgSbTe_2$ phase appeared from 450°C up to 700°C, which is different from the mixture phase of $AgInTe_2$ and Sb at the lower temperature. At the higher temperature the Ag-In-Sb-Te thin film seemed to be melted and when it was quenched about 100 degrees to 150 degrees the $AgSbTe_2$ phase was formed because $AgSbTe_2$ is a high-temperature phase[4] and its crystallization speed is very high compared to other phases[5]. This is the reason why $AgSbTe_2$ phase and amorphous phase co-exist in the initialized state. Moreover we can conclude that the initializing power must be high enough to heat the amorphous phase to slightly below the melting point of the thin film around 400°C where $AgSbTe_2$ phase is stable.

REFERENCE

1. H. Iwasaki, M. Harigaya, O. Nonoyama, Y. Kageyama, Jpn. J. Appl. Phys. Vol. 32 pp.5241-5247 Part 1, No. 11B, (1993)
2. Y. I. Kim and F. Izumi, J. Ceram. Soc. Jpn. 102 (1994) 401.
3. An Introduction to Crystal Chemistry. End Ed. R.C.Evans, Cambridge University Press, (1966), p.195
4. Pearson's Handbook of Crystallographic Data, p624
5. J.Tominaga etc. all, Jpn. J. Appl. Phys. Vol. 32 Part 1, No. 5A, May (1993) pp.1980-1982