X-ray analytics of amorphous and crystalline phases of GST/AIST Phase Change Materials

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ABSTRACT

Within a development project for the characterization of sputtered thin films for phase change optical disks, amorphous and crystalline phases of $Ge_2Sb_2Te_5$ (GST) and AgInSbTe (AIST) phase change materials have been investigated. Sputtered thin films (200nm) on polycarbonate were characterized before and after laser initialization using X-ray diffraction methods. The crystalline phase of GST was identified as fcc rock-salt like crystal structure ($Fm\bar{3}m$). The crystalline phase found in the AIST films was identified as the rhombohedral Sb phase. Rietveld refinements of structural parameters have been performed on ϑ-2ϑ measurements of thin films and powders.

Keywords: optical disk, phase change, phase transition, crystalline phase, X-Ray Diffraction, $Ge_2Sb_2Te_5$, AgInSbTe, structural parameters, Rietveld refinement

1. INTRODUCTION

In today's multimedia society, the demand of high-speed and high-density optical recording media using a direct overwrite scheme is very high. Phase change materials such as GeSbTe (GST) or AgInSbTe (AIST) alloys show a strong dependence of their optical properties upon their structure. They allow a reversible phase transformation with speeds of less than 100ns between the stable crystalline and amorphous phase. A focused laser beam is employed for this reversible transformation of individual bits.

The use of new materials and technologies requires higher standards and much tighter specifications for manufacturing of phase change optical disks. Engineering and process know-how together with an understanding of the physics behind the phase change processes are necessary for a successful development of a sputter tool for the manufacturing of DVD-ReWritables. The work presented here was performed within a development project together with Memex Optical Media Solutions AG in Zuzwil, Switzerland. The goal of the project was the development of analytical concepts and measurement procedures for the characterization of sputtered thin films for phase change optical disks. Measurements of layer thickness uniformity, characterization of the optical film properties (n&k) as well as measurements of thermal and mechanical layer stress were performed for selected materials. Further more the crystallization behavior of phase change stacks was investigated. Besides AFM microscopy for topographic analysis, stylus profilometry for measurements of layer thickness uniformity and reflection spectrometry for optical characterization of the thin films, x-ray diffraction methods were used for stress measurements and phase analysis.

X-Ray Diffraction (XRD) is used for phase analysis of polycrystalline materials that show characteristic Bragg-diffraction peaks at specific locations (2ϑ values) depending on their inherent crystalline structure. The X-ray pattern (diffractogram) is used to identify different crystalline phases or deduce elementary compositions of compound materials. For the characterization of typical phase-change materials such as AIST (for CD-ReWritables) or GST (for DVD-ReWritables) only few data exist. Therefore, literature values of quite recent papers have to be used for data analysis. The amorphous and the crystalline phases in sputtered AIST and GST thin films (200nm) on polycarbonate were investigated. The phase transition of the amorphous (as deposited) layer occurs during a laser initialization process. The resulting crystalline phases were measured using ϑ-2ϑ measurements on 200nm thin films and powders. The goal of these measurements was a test of the initialization procedure and the proof of a well defined crystalline phase.

2. EXPERIMENTAL PROCEDURE

A two layer structure consisting of 100nm ZnS-SiO_2 and 200nm of phase change material (GST / AIST) was deposited on a 0.6mm polycarbonate DVD-RAM substrate. The sputter deposition sequence was done on a Memex Wave 2-5 sputter tool. After the deposition, parts of the disk were initialized using a laser-crystallizer. Therefore, different positions on the same disk could be used to perform XRD-measurements of the amorphous and the crystalline phase change films. The sputtered amorphous ZnS-SiO_2 layer did not give any contribution to the GST / AIST diffraction pattern. For comparison X-ray diffractograms of 200nm films still on the substrate were compared with powder samples that were prepared by scraping off mechanically the deposited material of one entire disk.

The measurements were performed on a Philips X-ray diffractometer (PW 1050) operated at 40kV and 40mA. Cu-radiation (Cu Kα, λ=1.5418Å) without primary monochromator has been used. Data were collected in Bragg-Brentano mode within the range $20° < 2\vartheta < 80°$. The structural parameters of Ref. [3] were taken as starting values for a Rietveld refinement of the GST data. Reference values for the AIST system were taken from ICDD cards (International Center for Diffraction Data) [1]. Data analysis, Rietveld refinements, and pattern simulations were done using Philips Xpert-Plus software [7].

3. RESULTS AND DISCUSSION

3.1 X-RAY ANALYSIS OF THE GST-SAMPLE(S)

The XRD measurement results of the 200nm thick $Ge_2Sb_2Te_5$ disk sample are shown in Fig. 1. In a first step (Fig. 1a), a pure polycarbonate substrate was measured to characterize the background properties of the sample. Figures 1b and 1c show the measurements performed on the amorphous and crystalline part of the disk. From the background measurement, a systematic background correction for further data analysis seems justified.

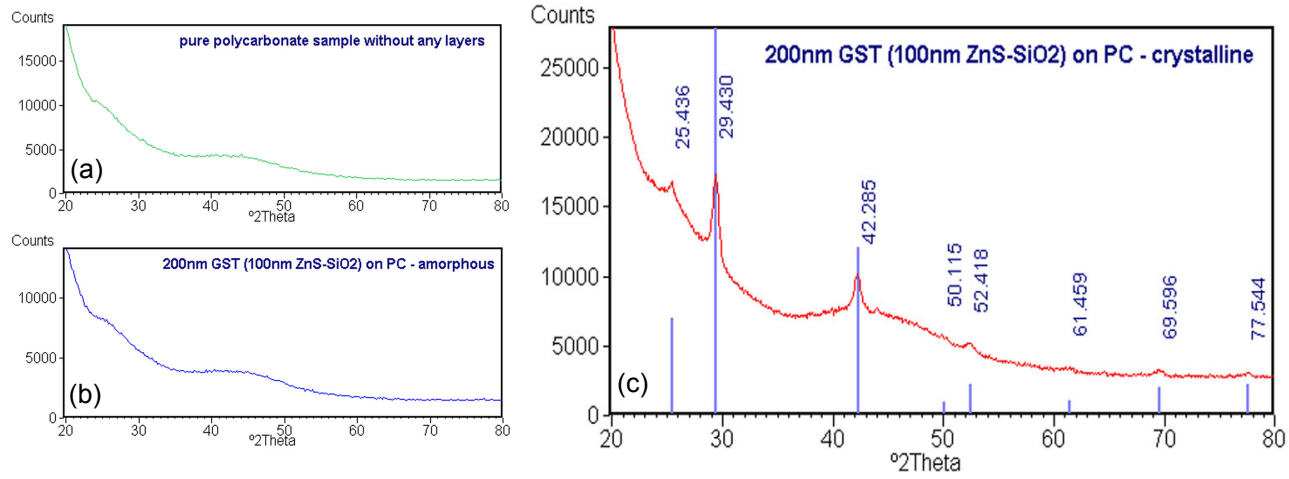

FIG. 1. XRD diffraction patterns of 200nm thick $Ge_2Sb_2Te_5$ films on 100nm ZnS-SiO_2 and polycarbonate. (a) Shows the background measurement on pure polycarbonate without any layers, (b) of the amorphous GST phase and (c) of the crystalline rock salt structure of $Ge_2Sb_2Te_5$.

A first analysis of the characteristic peaks of the crystalline GST phase in Fig. 1c clearly indicates a rock salt like structure. For the measured $Ge_2Sb_2Te_5$ phase, ICDD data are not yet available. For that reason a comparison of the measured diffractogram with GST literature values was performed. In Ref [2] the $Ge_2Sb_2Te_5$ structure was studied with X-ray diffraction after different annealing procedures. A clear structural transformation from the rock salt structure to the more complex hexagonal unit cell was observed. Furthermore, the authors observed a reduction of the lattice constant *a* of the cubic cell with increasing annealing temperature. In Ref. [3] the crystal structure of GeTe and GeSbTe phases was studied. The structural parameters taken from this paper served as starting values for a Rietveld refinement of our XRD-patterns. Fig. 2. shows the XRD profile of Fig. 1c after background correction. The red and the black curve show the results of measurement and calculation by the Rietveld refinement method. The blue lines indicate position and amplitude of the observed Bragg peaks. The lower box shows the difference signal between measured and calculated pattern. During the

refinement process, the lattice constant *a* (with *a*=*b*=*c*) is matched. The value R_{wp} (R-weighted pattern) is used to estimate the agreement between the observations and the model during the course of the refinement (5%<R_{wp}<10%: very good agreement; 10%<R_{wp}<20%: typical). A comparison of measured and literature values of rock salt like $Ge_2Sb_2Te_5$ phases is given in Table 1.

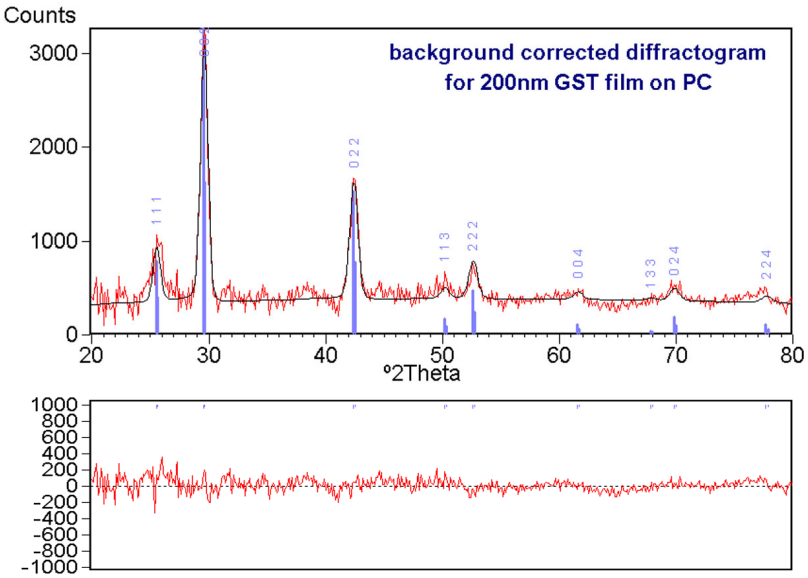

FIG. 2. XRD diffraction patterns of 200nm thick $Ge_2Sb_2Te_5$ films on 100nm ZnS-SiO_2 and polycarbonate. The red and the black curve show the results of measurement and calculation by the Rietveld refinement method. The lower curve shows the difference between measured and calculated profile.

To estimate the quality of the thin film data, powder XRD measurements on $Ge_2Sb_2Te_5$ were done for comparison. The crystalline material of one entire disk was used for analysis. Fig. 3. shows the measured powder XRD profile. The much better signal to noise ratio is due to the larger amount of GST material.

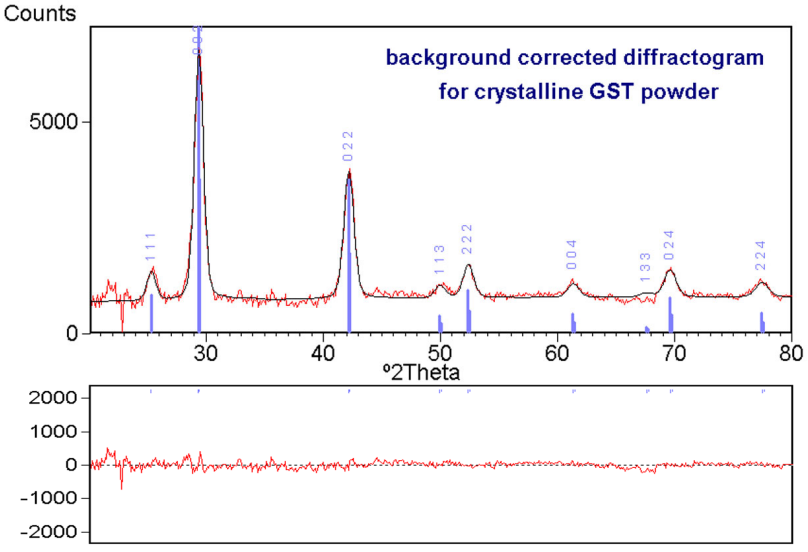

FIG. 3. Powder XRD pattern of $Ge_2Sb_2Te_5$. The red and the black curve show the results of measurement and calculation by the Rietveld refinement method. The lower curve shows the difference between measured and calculated profile.

After background correction the same analysis procedure as for the thin film sample was performed. The red and the black curve show the results of measurement and calculation by the Rietveld refinement method. The blue lines indicate position and amplitude of the observed Bragg peaks. The lower box again shows the difference signal between measured and calculated pattern. The obtained values for the lattice constant *a* and R_{wp} are given in Table 1.

A comparison of the values for the different samples shows good agreement for the lattice parameter. The Rietveld refinement of our GST films has been performed using an NaCl structure with the same amount of vacancies (20%) on the Ge/Sb-site as given in Ref [3]. The quality of our X-ray data did not allow us to refine the composition properly, however, as judged from the matching of the profiles, the composition of the crystalline phase in our GST film may be $Ge_{1.6}Sb_{1.6}Te_5$ (as in Ref. [3]) rather than $Ge_2Sb_2Te_5$. The same cubic phase was identified for 200nm film and powder samples.

Table 1.

Summary of the results for the lattice parameter *a* of the $Ge_2Sb_2Te_5$ rock salt structure and the R_{wp} value of the Rietveld refinement method

Sample	Lattice parameter (space group $Fm\bar{3}m$)	R_{pw} [%]
	a [Å] *(a=b=c)*	*R weighted profile*
REF [2]	**6.0117(5)**	12.5
200 GST film	**6.011(7)**	19.6
GST powder	**6.018(3)**	10.2

3.2 X-RAY ANALYSIS OF THE AIST-SAMPLE(S)

The XRD profiles of the 200nm thick AgInSbTe disk sample are shown in Fig. 4. Figure 4a shows the background measurement on the pure polycarbonate substrate. Figures 4b and 4c show the measurements performed on the amorphous and crystalline part of the AIST disk.

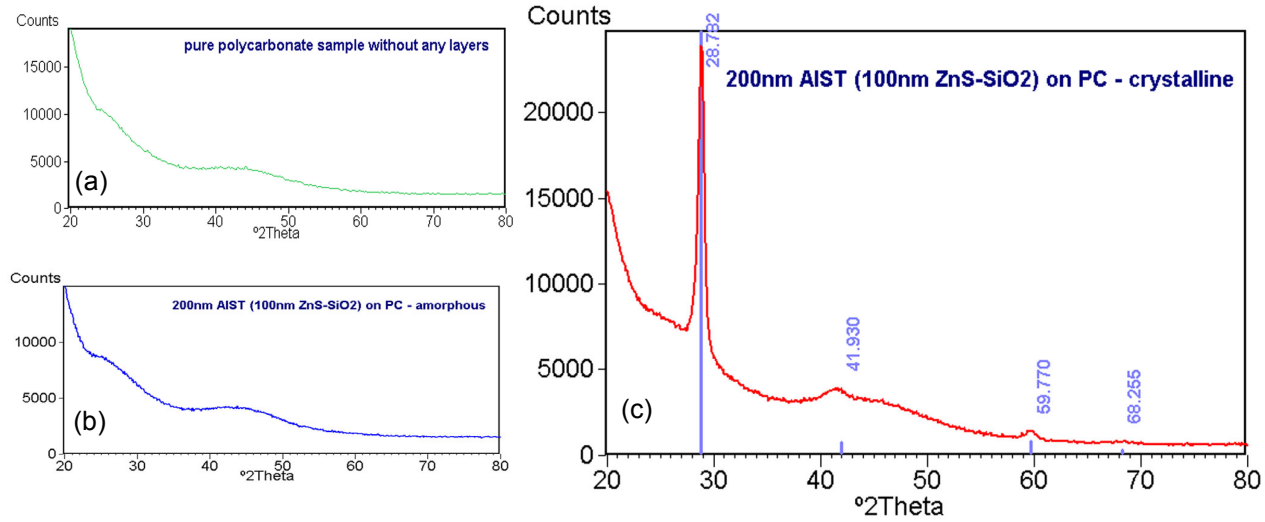

FIG. 4. XRD diffraction patterns of 200nm thick AgInSbTe films on 100nm ZnS-SiO_2 and polycarbonate. (a) Shows the background measurement on pure polycarbonate, (b) of the amorphous AIST phase and (c) of rhombohedral Sb phase of initialized AgInSbTe.

A comparison of the characteristic peak profile of crystalline AIST in Fig. 4c with available ICDD data (ICDD card no. 35-0732) indicates the presence of the rhombohedral Sb phase. Following Ref [4] and [5], this Sb phase is typical for laser initialization as well as temperature annealing procedures. Other possible crystalline phases of compounds like $Sb_{0.4}Te_{0.89}$, Sb_2Te_3 or $AgSbTe_2$ / $AgInTe_2$ (Ref [6], [5]) only match poorly with the experimental pattern.

For better phase identification and experimental resolution, an AIST powder measurement with long measurement time (80s/point; 0.1° steps) was performed. The larger amount of AIST powdered material together with an enhanced signal to noise ratio and the absence of texturing effects gave rise to additional peaks. Fig. 5. shows the XDR profile of the powder measurement after background correction. Very small grain sizes and lattice strain effects (compare also Ref [4]) may be reasons for the broad peak profiles in the observed patterns. Due to these effects, neighboring peaks merge and can no longer be resolved experimentally. Under these conditions, a Rietveld refinement is no longer reasonable. We therefore did a simulation of the expected Sb phase and compared it with the observed pattern. The red and the black curve show the diffraction pattern as measured and simulated using the Philips-Xpert Plus software. The blue lines indicate position and amplitude of the calculated Bragg peaks. The experimental data match reasonably well with the rhombohedral Sb phase

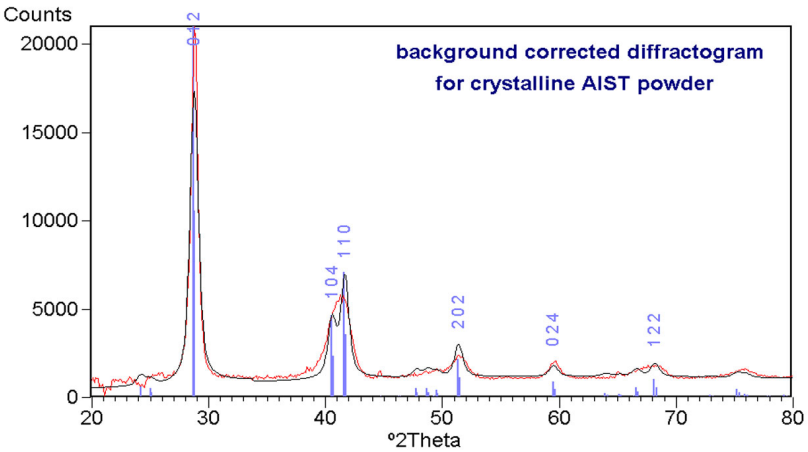

FIG. 5. Powder XRD pattern of AgInSbTe. The red curve shows the observed (background corrected) pattern. The simulated profile of the Sb rhombohedral phase is indicated by the black line. The blue lines show the position and amplitude of the calculated peaks.

4. SUMMARY

Within a development project together with Memex Optical Media Solutions AG, different kinds of analytical concepts and measurement procedures for the characterization of sputtered thin films for phase change optical disks have been developed. Using X-ray diffraction methods, the amorphous and crystalline phases of GST and AIST phase change materials have been characterized using reference values and the Rietveld refinement method. After a laser initialization process the crystalline phase of $Ge_2Sb_2Te_5$ was identified to be a defect cubic rock salt type structure with a lattice constant of about a=6.011Å and approx. 20% vacancies on Ge/Sb-sites. The crystalline phase in AgInSbTe films was found to be the rhombohedral Sb phase.

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