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Characterization of Ge–Sb–Te thin films deposited using a composition-spread approach

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Abstract

Ge–Sb–Te Thin films for rewritable phase change optical data storage applications were deposited by magnetron sputtering using a composition-spread approach. The deposition took place in an UHV chamber by cosputtering of three magnetron cathodes equipped with pure Ge-, Sb- and Te-targets in a DC–argon plasma. To investigate the influence of the chemical composition of the phase change material on its optical properties, films with lateral compositional gradients of up to 30 at.% were deposited. The composition, binding states and structure of the films were investigated by EPMA mappings, XPS, AES, RHEED and GIXRD on plain Si wafers, whereas the phase change velocity of Ge–Sb–Te was determined on Si–Al–SiO_2 stacks. The change between amorphous and crystalline phases of the films was induced and characterized with a static tester consisting of an optical microscope with an integrated high power laser diode. The change in reflectivity induced by the laser pulses was measured by a high sensitivity photo detector. Depending on the composition, the duration for the initial crystallization was determined between 220 and 500 ns, while the re-amorphization required between 20 and 120 ns. Structural analyses proved the existence of two crystalline phases with cubic and hexagonal structure in the initialized films.

Keywords: Combinatorial methods; Composition spread; Physical vapor deposition; Ge–Sb–Te

1. Introduction

Combinatorial synthesis and screening [1,2] is an established technique in pharmaceutical industry. Recently combinatorial approaches have been made to the screening of superconductive, magnetoresistant and photoluminescent materials [1]. In contrast to the complex masking techniques, which are usually used in combinatorial materials development [1], the composition-spread approach for materials development [3,4] is much less established. In this approach, two or three magnetron cathodes are adjusted to the sample under a low angle (Fig. 1) resulting in a film with a one- or two-dimensionally graded compositions. In combination with an analytical technique with high lateral resolution, a fast examination of the process window of thin films or coatings is possible. This approach has recently been successfully applied to the development of dielectric materials [5] and to the optimization of the oxidation resistance of metastable multicomponent hard coatings for cutting applications [6,7]. To investigate the suitability of the composition-spread technique for the optimization of optical data storage media, the present study was undertaken. The phase change velocity of Ge–Sb–Te with a composition around $Ge_2Sb_2Te_5$, manufactured by magnetron cosputtering of separate Ge, Sb and Te targets was evaluated as a function of composition.

2. Experimental

2.1. Deposition of the Ge–Sb–Te films

Ge–Sb–Te films were deposited from separate Ge, Sb and Te targets on Si(111) wafers and on Si(111)/Al/

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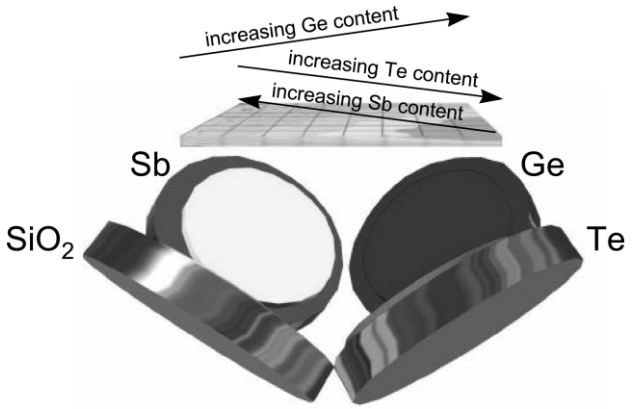

Fig. 1. Arrangement of the cathodes and resulting compositional gradient of the films.

SiO_2-multilayers in a magnetron sputtering system equipped with four cathodes whose arrangement is shown in Fig. 1. The cathodes are positioned on a 150-CF-Flange with a fixed tilt angle of 26° to the flange axis. The distance from the targets to the center of the substrate is 80 mm. The residual gas pressure of the system is $<1\times10^{-5}$ Pa. The multilayers were deposited in a Leybold L560 reactive magnetron sputtering system prior to the deposition of Ge–Sb–Te. The deposition parameters of the films are summarized in Table 1. The purity of all target materials and gases except for argon was 99.999%. Argon was used with a purity of 99.996%.

2.2. Characterization of the films by EPMA and XRD

Electron probe micro analysis (EPMA) elemental mappings and line-scans were carried out in a Camebax SX50 microprobe with four wavelength dispersive spectrometers at a primary energy of 15 keV. The relative accuracy for quantitative microanalyses is 1–5%.

Structural analyses of the films were carried out by X-ray diffraction (XRD) in a Siemens D 500 diffractometer with grazing incidence attachment at an X-ray incident angle of 3° to the surface. Diffraction patterns were taken in the 2Θ range of 20–80° using Cu Kα radiation at an X-ray power of 900 W.

Table 1
Deposition parameters of the films

Film no.	Deposition time/min	$p(O_2)$/ Pa	p(Ar)/ Pa	$P_{(RF)}$/ W Si	$P_{(DC)}$/W			
					Ge	Al	Sb	Te
1	40	–	1	–	–	7.8	4.4	6.9
2 A	5	–	0.6	–	200	–	–	–
b	15	0.2	0.6	300	–	–	–	–
c	5	–	1	–	–	7.7	4.4	6.8

Films one and two were deposited on Si(111). Film two is a multilayer consisting of three sublayers a, b and c.

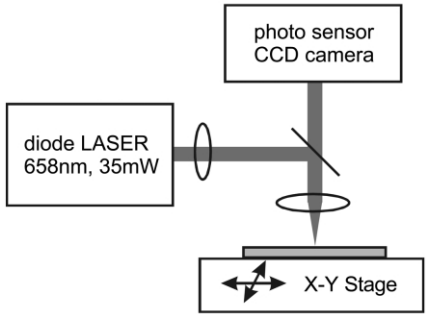

Fig. 2. Experimental setup of the static tester.

2.3. Characterization of the laser induced phase change of the films

The laser induced phase change from amorphous to crystalline Ge–Sb–Te films was studied in a static tester consisting of an optical microscope, a 658-nm laser diode and a silicon PIN photo diode as shown in Fig. 2. The phase change material is heated by a laser diode beam focused to a FWHM diameter of 0.7 μm. The incident power can be adjusted from 0 to 25 mW, the length of the laser pulses with a rectangular intensity profile from 10 ns to 1 s. The reflectivity of the irradiated area was measured by the detection of the reflected part of the laser beam with a silicon PIN photo diode. The sample position was controlled by an X–Y sample stage consisting of two step motors with a minimum step size of 0.5 μm. Additional information on the experimental setup can be found elsewhere [8,9].

When a laser pulse is applied, the layer is heated from ambient temperature to the maximum temperature T_{max} reached at the end of the laser pulse. After this, the surface temperature decreases due to heat flow into the substrate. A scheme of this process using pulses of different lengths and intensities is depicted in Fig. 3.

Two temperature levels can be distinguished, the crystallization temperature T_{cryst} and the melting temperature T_{melt}. If the laser pulse is too short, T_{cryst} is

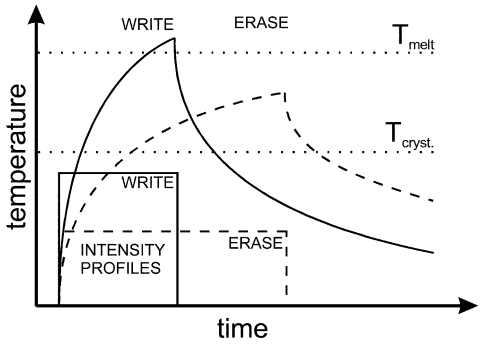

Fig. 3. Pulse profiles for writing and erasing processes.

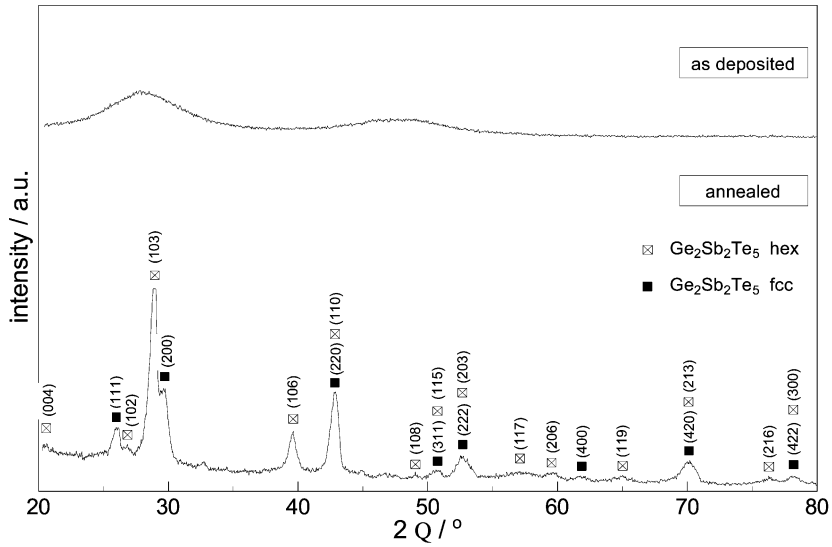

Fig. 4. The XRD patterns of Ge–Sb–Te film one.

never reached during the process and the phase change layer remains unaltered after a laser pulse. If the intensity and pulse width are both fitted so that $T_{cryst} < T_{max} < T_{melt}$, the irradiated area is transformed to crystalline Ge–Sb–Te. The reflectivity change by laser treatment between amorphous and crystalline Ge–Sb–Te was $\Delta R_{max} = 20\%$. The phase change layer is initialized or erased. If the intensity and pulse width are both fitted so that $T_{max} > T_{melt}$, the irradiated area is transformed to molten Ge–Sb–Te. If the rate of the subsequent cooling

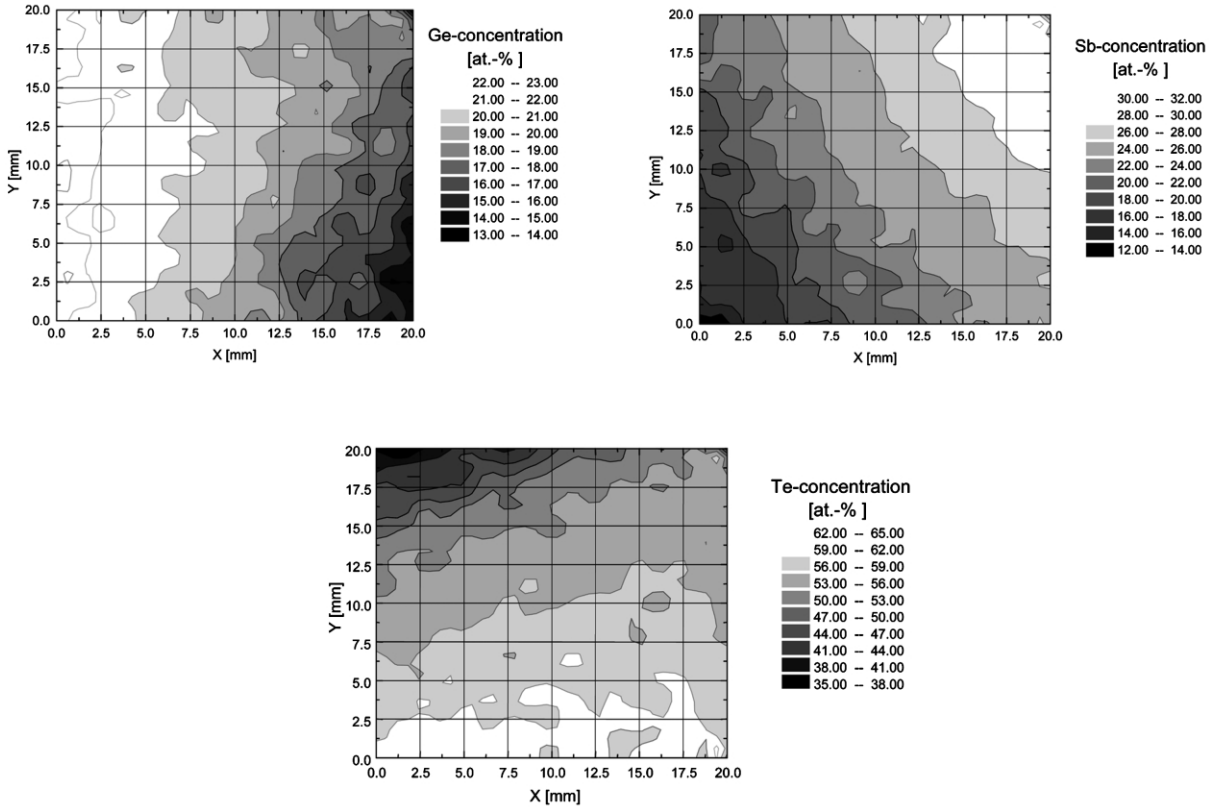

Fig. 5. The EPMA mappings of the laterally graded Ge–Sb–Te film one.

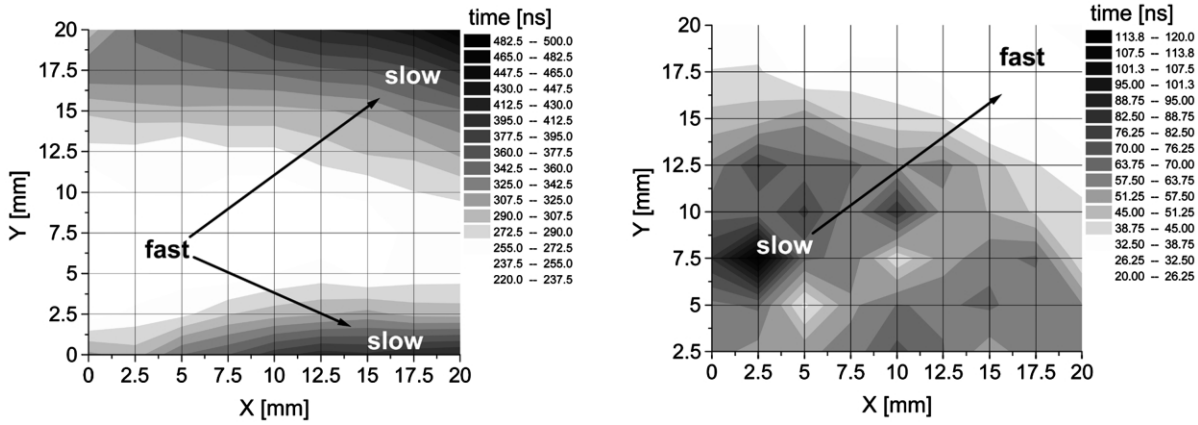

Fig. 6. *Left*: mapping of the crystallization time on the laterally graded film one. The step size between each measurement was 2.5 mm, the laser power 5.33 mW. *Right*: mapping of writing time on the laterally graded film two with an equivalent composition as compared to film one but an additional Al/SiO_2 layer as a heat sink. The step size between each measurement was 2.5 mm, the laser power 11.3 mW.

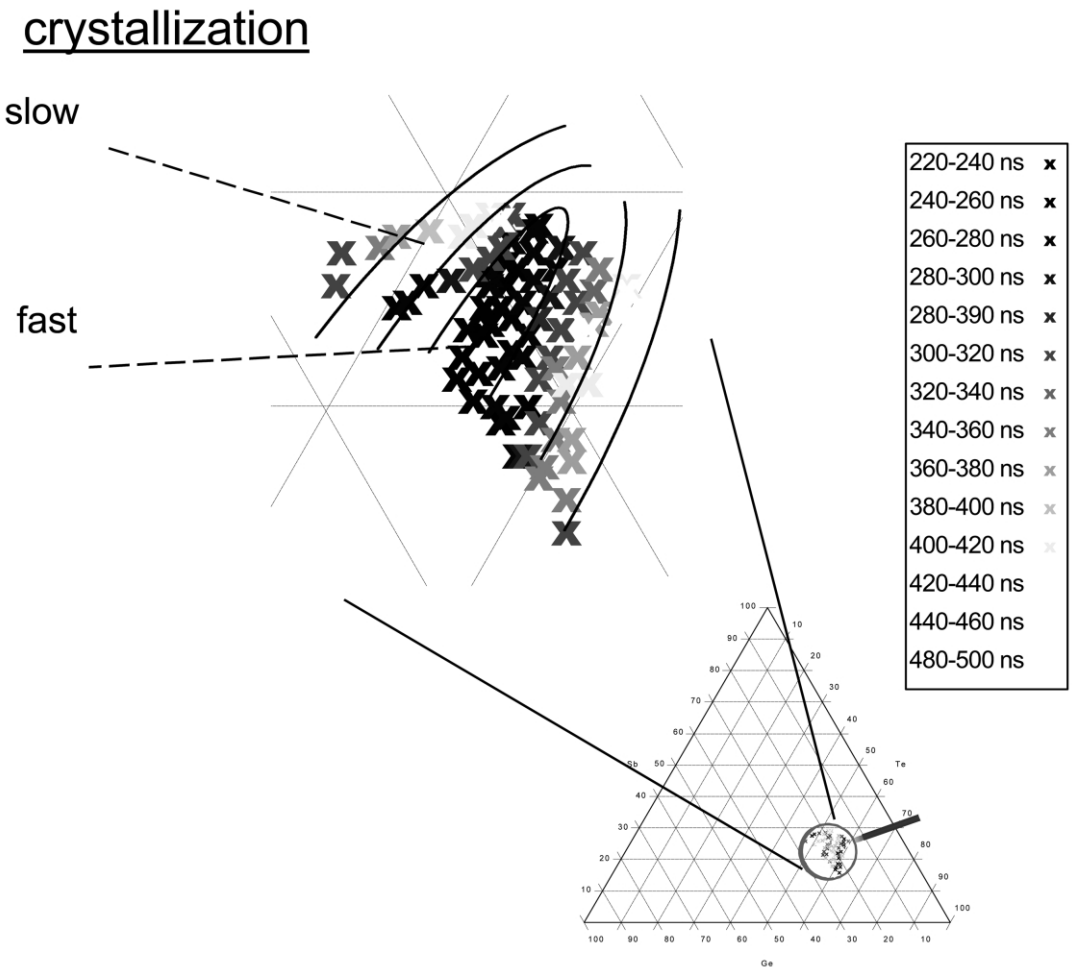

Fig. 7. Mapping of the crystallization time on the laterally graded film one as a function of composition (laser power 5.33 mW).

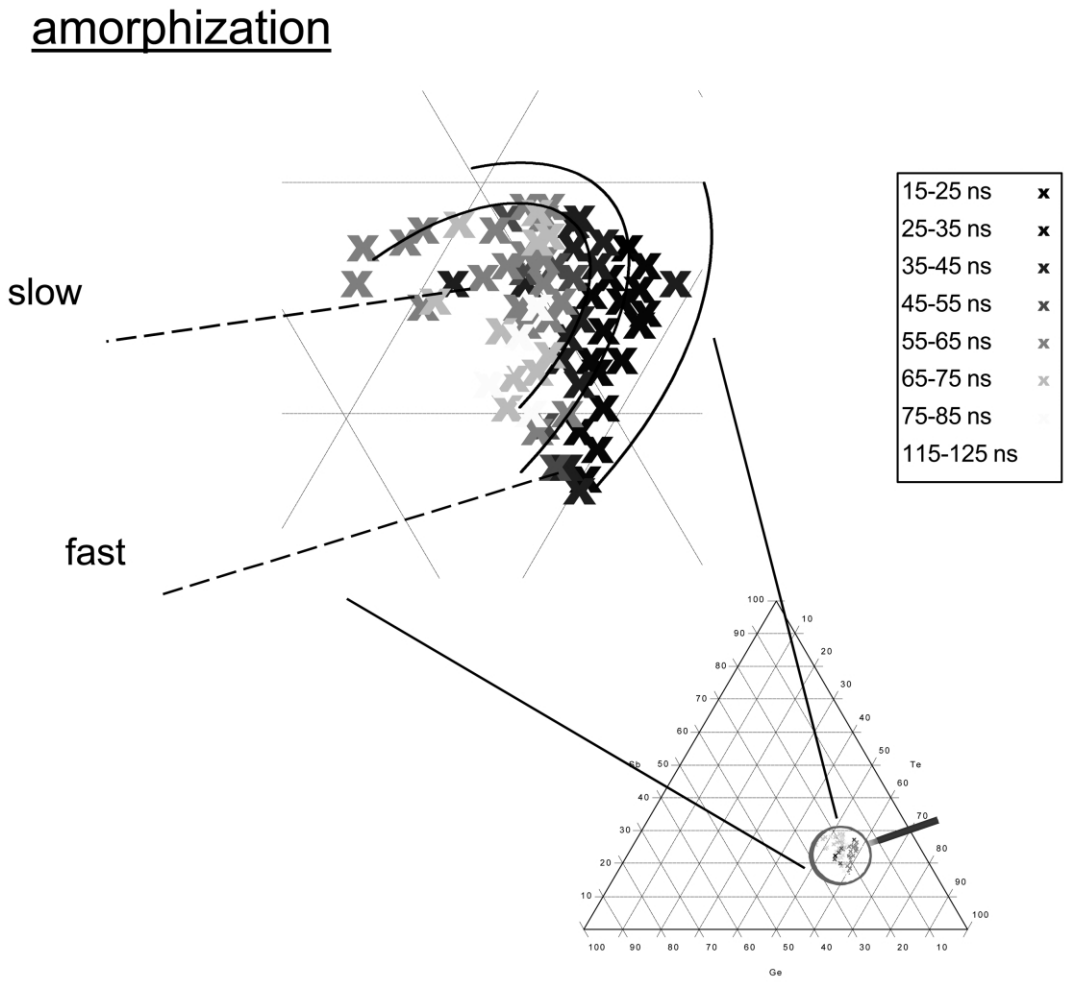

Fig. 8. Mapping of writing time on the laterally graded film two with an equivalent composition as compared to film one but an additional Al/SiO_2 layer as a heat sink as a function of composition (laser power 11.3 mW.)

is high, the disordered structure of the molten phase is quenched to an amorphous phase. The transition from the crystalline to the amorphous phase is called the writing process.

3. Results and discussion

The structure of the films was examined by means of XRD. The XRD measurements have been performed on as deposited coatings and after annealing in a vacuum chamber at 4×10^{-4} Pa. All films were deposited in amorphous state. After annealing for 10 min at 350°C, both cubic ($a=0.5990\pm0.004$ nm) and hexagonal ($a=0.4218\pm0.002$ nm, $c=1.79\pm0.06$ nm) $Ge_2Sb_2Te_5$ were detected (Fig. 4). This observation has been previously reported in literature [10,11].

For quantitative analyses of the films EPMA element mappings were carried out. Fig. 5 shows the EPMA mapping of a Ge–Sb–Te film with a lateral compositional gradient of up to 30 at.% for each element around the ternary $Ge_2Sb_2Te_5$ phase which is located near to the center of the wafer.

Fig. 6 shows a mapping of the crystallization time of film one. The mapping was performed in the same rectangular area of 20×20 mm as given in the EPMA mappings (Fig. 5). The distance between each position was 2.5 mm. Using a laser power of 5.3 mW and a focus diameter of 0.7 μm FWHM, the as deposited amorphous phase changed to the crystalline phase. The area of fast transition, i.e. low crystallization time (white color) corresponds with a composition of approximately $Ge_2Sb_2Te_5$.

The writing process depends on a high cooling rate. To grant this, a heat sink layer consisting of an aluminum film, had to be integrated into the sample structure. A SiO_2 protection layer is also required to inhibit a contact of the Al film with Ge–Sb–Te. Fig. 6 shows a mapping of writing time of the laterally graded Ge–Sb–Te film two with an identical composition as film one. Film two was deposited on a multilayer sample consisting of a

Al/SiO_2 stacking on silicon. The mapping is the result of measurements in a rectangular area of 20×17.5 mm corresponding to the EPMA mapping in Fig. 5. The distance between each position was 2.5 mm. Using a laser power of 9.3 mW and the focus diameter of 0.7-μm FWHM the film changed from the crystalline to the amorphous phase. It was possible to affect a phase change on the whole sample. However, in the range of $Ge_2Sb_2Te_5$ the writing process is very slow. This effect is caused by the fast crystallization process, as shown in Fig. 6. To avoid this influence a better heat sink would be sufficient.

In Fig. 7, the mapping of the crystallization time of the composition spread given in Fig. 6 (left) is plotted as a function of the composition. The mapping of writing time on the composition spread two with an equivalent composition as compared to film one but an additional Al/SiO_2 layer as a heat sink is given in Fig. 8 as a function of composition. Obviously, the crystallization time increased from 220 and 500 ns, depending on the composition, while the writing time was between 20 and 120 ns. The area with fast crystallization time and slow amorphization time corresponded with a composition of $Ge_2Sb_2Te_5$. With increasing distance from this chemical composition, the crystallization time increased at a simultaneous decrease in amorphization time.

4. Conclusions

Ge–Sb–Te layers with a continuous compositional gradient of up to 30 at.% around the stoichiometric $Ge_2Sb_2Te_5$ phase were deposited by magnetron cosputtering of separate Ge, Sb and Te targets and characterized with respect to structure and composition. Grazing incidence X-ray diffraction after a heat treatment of the initially amorphous films revealed the existence of two different crystalline modifications of $Ge_2Sb_2Te_5$. Depending on the composition, the crystallization time was determined between 220 and 500 ns, the writing time between 20 and 120 ns. The area with fast crystallization time and slow amorphization time corresponded with a composition of $Ge_2Sb_2Te_5$. With increasing distance from this chemical composition, the crystallization time increased at a simultaneous decrease in amorphization time.

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