***In-situ* crystallization of GeTe\GaSb phase change memory stacked films**

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Single and double layer phase change memory structures based on GeTe and GaSb thin films were deposited by pulsed laser deposition (PLD). Their crystallization behavior was studied using *in-situ* synchrotron techniques. Electrical resistance vs. temperature investigations, using the four points probe method, showed transition temperatures of 138 °C and 198 °C for GeTe and GaSb single films, respectively. It was found that after GeTe crystallization in the stacked films, Ga atoms from the GaSb layer diffused in the vacancies of the GeTe crystalline structure. Therefore, the crystallization temperature of the Sb-rich GaSb layer is decreased by more than 30 °C. Furthermore, at 210 °C, the antimony excess from GaSb films crystallizes as a secondary phase. At higher annealing temperatures, the crystalline Sb phase increased on the expense of GaSb crystalline phase which was reduced. Extended X-ray absorption fine structure (EXAFS) measurements at the Ga and Ge K-edges revealed changes in their local atomic environments as a function of the annealing temperature. Simulations unveil a tetrahedral configuration in the amorphous state and octahedral configuration in the crystalline state for Ge atoms, while Ga is four-fold coordinated in both as-deposited and annealed samples. © 2014 AIP Publishing LLC.

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I. INTRODUCTION

Due to modern technologies, the needs for storage capacity have increased exponentially. The most used memories today are nonvolatile memories. Among these, the most popular nonvolatile memories are Flash memories which are based on charge storage. Because charge storage memories are facing miniaturization problems,¹ some possible replacements are increasingly investigated. While magnetic and ferroelectric random access memories have problems with scalability,² the nonvolatile memories based on resistance change rather than charge storage seem to take the lead. In this class of resistive memories, we find phase change memories (PCMs). PCMs store data in a glass containing chalcogens (S, Se, or Te) or pnictogens (such as Sb) and use low voltage (or ultra-fast laser pulses) to switch subdomains of the material between two different states.³ In one state, the atoms of the glass are arranged in a disordered amorphous lattice (so called “off” state or digital “0”), while in the other state they have a crystalline distribution (“on” state or digital “1”). The transition from amorphous to crystalline is made using a pulse of intermediate power which locally heats the material above the glass transition temperature (T_g) and the material switches into the crystalline state. For phase change materials, T_g is only a few degrees below the crystallization temperature (T_x).⁴ This transition is accompanied by large variations in optical reflectivity (the refractive index is up to 30% higher in the crystalline phase) and electrical conductivity (the electrical resistance is several

orders of magnitude higher in the amorphous phase). Also, a decrease in sample thickness is produced (usually of a few percent, which will increase the material density). To switch a PCM memory cell back into the “off” state, a short intense pulse is used. The material is heated above the melting temperature and by rapid cooling (10^{10} K/s) it quenches into a disordered state. Usually, the crystallization is a slow process but due to the fact that phase change materials are poor glass formers⁵ they can be switched between these two states in a few nanoseconds. Several techniques such as *ab initio* molecular dynamics,⁶ Monte Carlo,⁷ and cellular automata⁸ have been used to model this transition.

Regarding the crystallization processes, there are two classes of phase change materials: nucleation dominated and growth dominated materials.⁵ In the first case, crystalline nuclei grow in the amorphous region while in the second case, the crystalline regions grow from the margins to the volume of the material. For phase change materials crystallization usually occurs at the interface. The nucleation dominated materials are characterized by long incubation times, while the nucleation sites are rare. The incubation time can be reduced by applying a weak electric field (0.3 V) to produce a pre-ordering of the amorphous clusters via Joule heating, leading to less than 1 ns switching times.⁹ Growth dominated materials are characterized by a strong dependence of the crystallization time on the size of the amorphous region, nucleation is very sparse and a supercritical nucleus size is needed in order for the crystallization to occur. After the formation of a crystalline nucleus, the crystallization proceeds through the rapid movement of the amorphous/crystalline boundary.

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In the last years, attention was turned to binary PCM like GeTe¹⁰ and GaSb¹¹ as promising candidates for technological applications since they combine high speed with good thermal stability. GeTe is a growth dominated material¹² with a crystallization time of a few nanoseconds¹³ achieved using Nd:YAG laser pulses and the and measured with optical microscopy and TEM near the crystallization temperature. It is considered one of the best materials for phase change memories.¹⁴ GaSb is a nucleation-dominated material, with a high thermal stability due to a very stable amorphous phase¹⁵ and a fast crystallization time (<15 ns obtained when heated to temperatures close to their melting point).¹⁶ GaSb shows negative optical contrast (i.e., the refractive index is smaller in the crystalline phase than in the amorphous one, which is not a typical aspect of phase change materials) upon crystallization, but this do not affect electronic memories. Sb is often proposed for replacing Te and has the potential to offer a fast phase transition due to minimal changes in the atomic rearrangement from the amorphous to the crystalline phase.¹⁷

What is exciting about PCMs is that multiple states can be recorded in a single PCM memory cell.^{18,19} There are several approaches to achieve this goal. One is to store multiple states in a single film phase change material by controlling the crystalline to amorphous ratio in the thin film. For example, AlSb²⁰ exhibits three distinct resistance levels due to the co-existence of crystalline Sb-rich regions in an Al-rich amorphous matrix. Unfortunately, this approach suffers from resistance drift²¹ over time and cannot ensure long time stability of the memory cell. Another approach is to stack different films of chalcogenide materials.^{22,23} Each state corresponds to a different value of the cell resistance and to a different combination of the layers structure. Because this second approach is more robust in terms of stability we chose to use it in our experiments.

An important drawback of phase change memory materials is void formation²⁴ during cycling due to the large difference in density between the two phases. This phenomenon leads to elemental segregation which is a common failure mechanism observed in PCM cells using GST (Ge₂Sb₂Te₅) as a phase change material. The defects induced in the material by these effects can be beneficial at the beginning, leading to an increase in the switching speed²⁵ but also to cell failure when a certain amount of the material is affected. Antimony-rich areas are usually formed near the electrodes²⁶ causing a reduced crystallization temperature and stability.²⁷

In order to better understand the crystallization process in stacked structures, we need to know the structure of the materials in the amorphous and crystalline states. This knowledge is critical in revealing the switching mechanism and is useful for improving materials properties. The amorphous state is not stable and is not unique. On the other hand, one would believe that resolving the crystalline structure of phase change materials is a straight forward process with all the modern techniques and should be much easier than for the amorphous phase. Due to the fact that phase change materials have crystallization speed of a few nanoseconds, their crystalline state consists of small crystallites (tens of nanometers)

without any preferred orientation. That is why the crystalline phases are usually metastable and they have a lot of similarities with the amorphous phases from whom they originate. This kind of polycrystalline domains lead to low intensity broad diffraction peaks. An idea to solve this problem of structure determination was to investigate single crystals²⁸ and resolve their structure but then comes the question of how much resemblance is between single crystals grown close to thermal equilibrium and polycrystalline materials obtained on timescales of nanoseconds and fast cooling rates. Another solution for structure determination, which we have adopted here, is to simultaneously measure by two complementary techniques (Extended X-ray Absorption Fine Structure—EXAFS and X-ray Diffraction—XRD) the short and long-range order during the phase transition. Combined synchrotron techniques like EXAFS and XRD are great tools for the *in-situ/ex-situ* determination of the local structure around the absorbing atom such as the number of nearest neighbors, their chemical nature, the interatomic distances and the disorder in both the amorphous and the crystalline states. In this paper, we report a comparative study regarding the crystallization behavior of single and stacked films of GeTe and GaSb.

II. MATERIALS AND METHODS

Pulsed laser deposition (PLD) was proved to be a successful method for preparing chalcogenide films with similar stoichiometry as the targets,²⁹ on large uniform areas.³⁰ It is used for obtaining a broad range of amorphous thin films applicable in optoelectronics,³¹ chemical sensors,³² optical waveguides,³³ and phase change materials.³⁴ We believe that PLD is a scalable, versatile, and cost effective method which can be used to grow high quality phase change samples in a very short time. The deposition method should always be taken into account in the case of phase change materials due to the influence on the microstructure and the crystallization temperature, which control the optical and electrical properties of the samples. In some cases, the crystallization temperature of thin films with the same composition of the initial target present differences larger than 200 °C for various deposition methods and no explanation has been found yet.³⁵ The deposition was carried out using a KrF* laser source, model COMPexPro 205, Lambda Physics-Coherent ($\lambda = 248$ nm, $\tau_{FWHM} = 25$ ns). The targets were irradiated using a 10 Hz repetition rate and a laser fluence of 1.5 J/cm². The depositions were carried out at room temperature and the pressure inside the deposition chamber was 5×10^{-4} Pa. During laser irradiation, the substrates were kept at room temperature. The target-substrate separation distance was 4 cm for GeTe films and 8 cm for GaSb films in order to avoid as much as possible the formation of droplets, taking into account that GaSb is a softer material than GeTe. Due to the difference in the target-substrate separation distance and hardness of the materials, different numbers of laser pulses were used in order to obtain the desired film thicknesses (7500 and 20 000 pulses for GeTe and GaSb, respectively).

PLD targets were prepared using high purity powders (5N GeTe and 4N GaSb), from Alpha Aesar, which were

loaded in vacuum evacuated quartz ampoules and melted for 2 h at 800 °C in a tubular rocking furnace. Finally, the ampoules were slowly cooled until room temperature in air. Thus, ingots of 10 mm in diameter and 20 mm in length were obtained and then cut as discs of 2 mm thickness. In order to provide a good adhesion for the chalcogenide films but also to be transparent as much as possible to X-rays, 200 μm thick glass substrates were used. Film thickness and roughness were measured using a non-contact Veeco Dektak 150 profilometer. We obtained films with thicknesses ranging between 200 and 500 nm and a roughness between 20 and 50 nm. Thickness is another factor which influences the crystallization temperature of phase change materials.³⁶ It becomes very important for films with thicknesses below 10 nm, leading to an increase of more than 200 °C of the crystallization temperature. For thicknesses above 10 nm, the crystallization temperature is more or less the same as compared to the bulk samples. The average composition of the films was measured by means of an X-ray Fluorescence table top system from EDAX, using a beam size of 2 mm² and an acquisition time of 200 s. The radiation was produced by an Rh cathode using an accelerating voltage of 35 kV and a current of 200 mA. The sample composition is very important for the properties of thin phase change memory films. For example, the crystallization time is several orders of magnitude different for small changes in the material composition³⁷ and is very different for as-deposited as opposed to melt quenched samples.³⁸ The films obtained in this study were uniform in thickness and composition on an area of 2.5 cm².

Electrical resistance versus temperature measurements were performed in a custom-made four-point measurement setup using Pt sputtered contacts on film surfaces. The measurements were conducted in Ar atmosphere using continuous heating at a rate of 4 °C/min. The heating rate is another parameter that influences the crystallization temperature. Thus, an increase in the crystallization temperature of more than 20 °C, when the heating rate was increased from 0.5 to 5.3 °C/min, was observed.³⁹ XRD and EXAFS measurements were performed at the microXAS beamline⁴⁰ from the Swiss Light Source. *In-situ* X-ray diffraction was carried out using a hot air blower with a heating rate of 10 °C/min. Additional X-ray diffraction measurements were performed on samples annealed *ex-situ*, in Ar atmosphere, at temperatures below and above the transition temperatures of the single layers. The heating rate in this case was 4 °C/min and a 2 h plateau. In order to detect most of the diffraction peaks, XRD spectra were acquired using high energy radiation (17 keV, $\lambda = 0.729 \text{ \AA}$), from a monochromator with Si (111) crystals and a small area single photon counting bi-dimensional detector (100 k Pilatus, DECTRIS Ltd.) situated at 5 cm from the sample. The diffraction patterns were collected in transmission geometry and the observed 2θ range was between 10 and 45°.

For the computation of crystallite size and microstrain, we used Williamson-Hall analysis.⁴¹ The peak broadening (β) of a reflection located at a 2θ angle is given by the following formula:

$$\beta = \frac{K\lambda}{D \cos(\theta)} + \varepsilon \tan(\theta), \quad (1)$$

where K is Scherrer's constant, λ the wavelength, θ the angle and ε is related to the microstrain and D is the crystallite size. By plotting $\beta \cos(\theta)$ as a function of $\tan(\theta)$, a straight line is obtained. The microstrain occurring between crystallites is inferred from the slope of this line, while the average crystallites size is determined from the intercept. Gaussian convolution of the experimental peak profiles and a value of 0.9 for the Scherrer constant were used. EXAFS spectra were collected in fluorescence mode on the *ex-situ* annealed samples using a single element Si drift diode detector (from Ketek, 160 eV resolution). Investigations were performed at the Ga (10.36 keV) and Ge (11.1 keV) K edges. In both cases, the beam size was $300 \times 300 \mu\text{m}^2$. The XRD data were compiled and analyzed using XRDUA⁴² and Match⁴³ software packages, while the EXAFS data were analyzed using Demeter.⁴⁴ The simulations were performed using Artemis.

III. RESULTS AND DISCUSSION

Single films of GeTe and GaSb with thicknesses of 500 nm and 200 nm, respectively, as well as double layers of GeTe/GaSb (500 nm/200 nm) were produced by PLD. Roughness measurements showed that GeTe films were smooth with RMS values less than 20 nm, while the GaSb films were rougher with RMS values around 50 nm, mainly due to PLD droplets. The large area films we prepared together with the $300 \times 300 \mu\text{m}^2$ X-ray beam size, gave us the possibility to target the zones with the lowest concentration of droplets for XRD and EXAFS measurements. The composition of the single and stacked films measured by XRF with an error of $\pm 2\%$ is summarized in Table I. The samples are slightly non-stoichiometric with Ge and Sb, respectively, in excess.

A. GeTe

It is known that at temperatures below 430 °C, GeTe has a distorted rock-salt structure.⁴⁵ Ge and Te atoms occupy the cation lattice and the anion lattice positions, respectively. Due to the fact that these two lattices are shifted, the lattice angle decreases and the resulted structure is rhombohedral ($a = 8.342 \text{ \AA}$, $c = 10.668 \text{ \AA}$), R3m space group. Above 430 °C, a transition from the rhombohedral metastable crystalline structure to a rock-salt cubic structure occurs.⁴⁶ This additional transition (which was not achieved in the current experiments because lower annealing temperatures were used) is also accompanied by a drop in resistance (which is usually smaller than the first one) and very often by

TABLE I. Sample composition determined by XRF.

Sample	Ge (at. %)	Te (at. %)	Ga (at. %)	Sb (at. %)
GeTe	58	42	...	...
GaSb	...	...	46	54
GeTe/GaSb	58	42	46	54

elemental phase segregation. The mechanism of the structural arrangement during crystallization and amorphization is still unclear. In most amorphous solids, their short range order resembles the structure of their corresponding crystals. GeTe is an exception from this rule and its structure in the amorphous and crystalline states has not been entirely revealed. Another counterintuitive fact is that the Ge–Te bond is longer (i.e., weaker) in the crystalline state than in the amorphous structure.⁴⁷ In the amorphous phase both homopolar Ge–Ge and heteropolar Ge–Te bonds exist in the first coordination shells while after crystallization only Ge–Te bonds exist and they increase significantly in length. It was shown that in the amorphous state there is a random covalent network with Ge four fold coordinated and Te two fold coordinated,^{48,49} while others suggest that Ge and Te are both threefold coordinated.^{50,51} Some other authors do not agree with this theory and consider that the structure is a mix of 4(Ge):2(Te) and 3(Ge):3(Te) coordinated structural units.⁵²

For a precise determination of the crystallization temperatures in single films, we performed resistance versus temperature (R–T) measurements. Fig. 1 shows the results of the R–T measurements on the GeTe single films. At temperatures below, the crystallization threshold, the films were highly resistive due to their amorphous (insulating) phase and the resistivity decreased gradually until exceeding the crystallization/transition temperature. The conductivity in amorphous materials can be modeled by a thermally activated hopping process,⁵³ until a rapid drop in resistance is observed at the transition to the crystalline (conductive) state. The resistivity in the crystalline state does not depend on the annealing temperature because GeTe is a degenerate semiconductor.⁵⁴ In the case of our GeTe films, the drop in resistance is of 5 orders of magnitude and occurs at a transition temperature of 138 °C. A similar temperature was also reported by Kolobov *et al.*⁴⁷ for 5 μm thick films obtained by magnetron sputtering onto Kapton substrate. The crystallization temperature was

FIG. 1. Typical resistance–temperature measurements on GeTe thin films measured using the four points probe method. The films were measured in Ar atmosphere using continuous heating at 4 °C/min. Crystallization is indicated by a sudden drop in resistance at 138 °C.

determined from the peak in the first order derivative of the resistivity as function of temperature. Upon cooling, the sample remained in the low resistivity state because in our experiments the melting temperature of the material has not been reached and the transition back into the amorphous state was not possible.

Fig. 2 presents the XRD diffractograms recorded on the same GeTe thin films used for temperature–resistance measurements, before and after annealing. GeTe thin films were amorphous and they have crystallized in a rhombohedral structure after annealing. The crystallization is a one-step process characterized by the appearance of X-ray diffraction peaks at one temperature correlated with the sharp drop in resistance at the same temperature. The wide peak centered at $2\theta = 10.7^\circ$ is due to scattering from the glass substrate. The intensity of the diffraction peaks was normalized to 1 using GeTe (202) crystalline peak intensity for both as-deposited and annealed samples spectra. The appearance of Ge (111) and Te (012) peaks at high annealing temperature (250 °C) implies the presence of precipitation without any significant variation of electrical resistance. Ge precipitation was also observed by Raoux *et al.*⁵⁵ in the case of co-sputtered GeTe samples annealed above 200 °C. The Ge and Te precipitation is due to non-stoichiometric samples and long annealing times. Crystallite size and microstrain were computed using the Williamson-Hall analysis (detailed in Sec. II). For a better estimation only non-overlapping peaks were used. As one can see from the linear regression in Fig. 3, the slope gives a microstrain of 3.55×10^{-3} for rhombohedral GeTe and the intercept an average crystallites size of 15 ± 3 nm.

B. GaSb

GaSb has a face-centered cubic structure,⁵⁶ F-43 m space group, with a lattice constant $a = 6.095$ and an amorphous structure very similar with the crystalline state structure. In the amorphous state, Ga is surrounded by almost four (3.7) Sb atoms in the first shell, while in the crystalline state Ga has exactly 4 Sb neighbors.⁵⁶ This small difference

FIG. 2. Typical XRD spectra of GeTe films, before and after annealing at 250 °C. GeTe crystallizes into a rhombohedral structure (inset). Ge and Te phase segregation is observed in the annealed sample.

FIG. 3. Williamson-Hall analysis on GeTe films. The crystallites size is approximately 15 nm. Debye-Scherrer rings of as-deposited and annealed samples are shown in the inset.

is due to the presence of wrong Ga – Ga bonds in the amorphous phase.

For the gallium antimony sample the transition temperature is at 198 °C as shown in Fig. 4 and the electrical contrast is of 4 orders of magnitude. Upon cooling the resistance remains lower than in the amorphous phase. The electrical contrast in our GaSb films, which have slightly non-stoichiometric composition, is much stronger than the contrast in stoichiometric GaSb which was found to be of only one order of magnitude.⁵⁷ The electrical contrast can be increased by annealing at temperatures much higher than the crystallization temperature.²³ However, this is not a viable solution because high annealing temperatures induce an irreversible segregation process. Gallium antimony is partially crystalline in the as-deposited state and it fully crystallizes after the transition temperature as seen in Fig. 5. All peaks from the XRD diffraction can be identified as cubic GaSb phase. The XRD results are in agreement with the resistivity vs. temperature data. The partial crystallinity of GaSb films, which is mainly due to PLD droplets (SEM measurements showed droplets of

FIG. 4. Electrical resistance—temperature measurements on GaSb thin films measured using the four points probe method. The films were measured in Ar atmosphere using continuous heating at 4 °C/min. Crystallization is indicated by a sudden drop in resistance at 198 °C.

FIG. 5. XRD spectra of GaSb films, before and after annealing. GaSb crystallizes into a cubic structure (inset). Sb crystallization was observed in the annealed samples.

35–50 nm, data not shown), does not affect the switching effect. The fact that the crystallization temperature of our single layer GaSb films is so close to the value found in the literature (203 °C)¹¹ for films prepared using other techniques such as sputter deposition suggests that the influence of droplets is not important in our experiments. In the diffraction pattern, some small amount of metallic phase of Sb can be detected. The Sb (012) rhombohedral peak is present in the as-deposited films and increases at high annealing temperatures, where the second peak of the rhombohedral phase appears due to Sb excess crystallization. Raoux *et al.*¹¹ reported crystalline rhombohedral Sb in samples deposited at room temperature and observed Sb segregation at annealing temperatures as high as 350 °C. It was suggested¹¹ that materials with an excess of Sb could be of great interest for multi-state phase change materials due to their stepwise crystallization, the first step being the crystallization of GaSb at lower temperatures and the second step the crystallization of Sb at higher annealing temperatures. This second drop in resistance was not achieved in our experiments due to lower annealing temperatures. Sb precipitation was also found in GeSb films at high annealing temperatures.⁵⁸ A slight displacement of the diffraction peaks is evidenced in the annealed samples which could be attributed to density change after phase transition. The intensity of the diffraction peaks was normalized to 1 using GaSb (111) crystalline peak intensity for both as-deposited and annealed samples.

The negative slope in the Williamson-Hall plot (Fig. 6) indicates that the microstrain is minimal in the material.⁵⁹ Usually, the full width half maximum (FWHM) increases with $\sin(\theta)$ because the broadening due to microstrain must increase. In the case of GaSb single films FWHM decreases showing that microstrain is not a source of broadening, therefore it is very low. The intercept gives an average crystallites size of 8.5 nm $\pm$ 1.5 nm. This estimation of crystallite size indicates a continuous nucleation process in the case of GaSb as reported also in the literature. An estimation of the lattice constant from the XRD spectra is 6.065 $\pm$ 0.002 Å before annealing and 6.100 $\pm$ 0.002 Å after annealing, which is very close to the published value.⁵⁶

FIG. 6. Williamson-Hall analysis on GaSb thin films. The average crystallite size is approximately 9 nm and does not change from the as-deposited to the annealed samples.

C. GeTe/GaSb

In order to investigate the possibility of controlling the crystallization of the individual layers, we performed *in-situ* X-ray diffraction vs. temperature measurements on GeTe/GaSb stacked structures. Fig. 7 shows that GaSb is partially crystalline at room temperature which was also the case for single films. Further increase in temperature determines the appearance of GeTe rhombohedral peaks after 155 °C. Crystallization temperature was estimated by integrating the area of GaSb (111) and GeTe (202) diffraction peaks as a function of temperature and computing the first order derivative maximum. The increase in peak area, due to peak broadening caused by the reduction of grain size or film thickness, was not considered. The crystallization temperatures derived from XRD are usually 10–20 °C higher compared to electrical vs. resistance measurements. The reason for this is that XRD peaks require a substantial fraction of the material to be in long range ordered crystalline state, while the drop in resistivity requires only the existence of a

conduction filament between the electrodes which does not depend on ordered paths.

Fig. 8 denotes a crystallization temperature of 150 °C for GeTe. After GeTe crystallization, we consider that some of the Ga atoms (which are the smallest atoms in the structure) diffused in the vacancies of the GeTe crystalline structure (the GeTe crystalline structure contains up to 10% vacancies). Diffusion produced an increased concentration of Sb in the GaSb film which will lead to a reduction of the crystallization temperature as shown by Raoux *et al.*⁶⁰ The crystallization temperature is composition dependent, decreasing with the increase in Sb concentration. Thus, the crystallization temperature of the Sb-rich GaSb layer is decreased to 168 °C. On the other hand, the interface might play a role in the crystallization of GaSb. GeTe droplets and the mismatch between lattice constants of the two films will lead to a stressed interface. This stress will increase after GeTe crystallization and could determine the formation of crystallization nuclei in the GaSb film. These nucleation sites might trigger the crystallization in the GaSb film. Furthermore, Sb, which is known to exhibit an explosive crystallization,⁶¹ begins to crystallize at 210 °C as shown by the arrow in Fig. 8. Sb (012) rhombohedral peak starts to be visible at this temperature and then increases with annealing. Further crystallization of antimony produces a drop in GaSb (111) peak intensity (Fig. 8), meaning that after Sb excess crystallizes then the crystalline Sb phase grows on the expense of GaSb phase which starts to separate. GaSb (400) peak intensity decrease could also be related to antimony crystallization. A similar result was found by Kaiser *et al.*⁶² They studied the crystallization of bulk Sb-rich alloys by transmission electron microscopy and showed that these alloys are not stable and they separate in GaSb and Sb. A analogous process was found in GeSb alloys. Del Pozo *et al.*⁶³ suggested a metallic induced crystallization for Ge precipitation at temperatures above Sb crystallization in GeSb alloys. The process begins with the crystallization of Sb and its diffusion into the GeSb matrix leading to Ge–Sb bond breaking and Ge crystallization.

FIG. 7. XRD spectra of GeTe/GaSb stacked films during *in-situ* annealing between 35 °C and 310 °C. GeTe crystallization occurs at 149 °C and Sb crystallizes at 210 °C. The crystallization of GeTe film is highlighted.

FIG. 8. Normalized integrated areas of GaSb (111) (green), GeTe (202) (brown) and Sb (012) diffraction peaks. The crystallization of GeTe activates the crystallization of GaSb, while Sb starts to crystallize at 210 °C leading to a decrease in the GaSb (111) peak.

FIG. 12. XANES spectra at Ga edge of GeTe/GaSb films, *ex-situ* annealed at 100 °C, 160 °C, and 250 °C. Changes in the white line intensity are observed in the samples annealed at 160 °C and 250 °C.

tetrahedral one. 10% of Ge vacancies are present in the Ge sublattice which is crucial for reversible phase change materials.³⁷ Such Ge vacancies and chalcogen lone pair electrons support this transformation. It is supposed that even in stoichiometric GeTe a quasi-amorphous germanium matrix is present in the crystalline state,⁴⁷ which gives rise to lattice distortions.⁶⁵

The structure in the local environment of Ga, shown in Fig. 12, is more or less the same in all annealed samples, because of the small difference in structure between the crystalline and amorphous states⁵⁶ and also due to the fact that the ratio of crystalline material in the as-deposited state compared to the sample annealed at 250 °C is 52%. The amount of crystalline material was computed by dividing the areas of the GaSb (111) diffraction peaks in the as-deposited sample and after annealing at 250 °C (Fig. 9). Small increases in the white line intensity correlated with a shoulder around 10.375 keV (denoted by an arrow) are signs of crystallization. The simulations shown in Fig. 13 were performed taking into account only the single scattering path given by 4 Sb atoms present in the first shell at a distance of 2.64 Å.⁵⁶ An amplitude reduction factor of 0.7 was fixed for all four simulations. The good agreement between simulations and data suggests that Ga is four fold coordinated in both as-deposited

FIG. 13. k^2 -weighted back-Fourier transformed EXAFS oscillations at Ga edge (solid lines) and GaSb structure simulations (dashed-dotted lines).

and annealed samples. Identical results were obtained for the single films (data not shown).

IV. SUMMARY

Crystallization of germanium telluride and gallium antimony single and stacked films, prepared using pulsed laser deposition, was successfully achieved. GeTe single films were amorphous in the as-deposited state and they crystallized after reaching the transition temperature, while GaSb films were partially crystalline in the as-deposited state mainly due to the unavoidable formation of PLD droplets, which does not affect the crystallization temperature of the single films. The samples were slightly non-stoichiometric, which actually helped GaSb to increase its electrical contrast up to four orders of magnitude. A small phase separation of Sb was observed in the as-deposited GaSb films due to Sb excess. Ge and Te segregations were found in the *ex-situ* annealed GeTe samples because of the long annealing times. The stacked films showed different characteristics than single films in terms of crystallization temperatures. After GeTe crystallization, Ga atoms diffused from the GaSb layer into the voids of the crystalline GeTe layer. This diffusion will lead to a remaining Sb-rich GaSb layer which has a lower crystallization temperature than its single film counterpart. At higher annealing temperatures, the antimony excess from the remaining Sb-rich GaSb layer crystallizes. The crystalline Sb phase increases on the expense of GaSb crystalline phase which is reduced. This segregation is unfavorable because it is irreversible and it will deteriorate the stability and reliability performance of PCM cells. EXAFS measurements and simulations revealed that Ge is four fold coordinated in the amorphous GeTe while in the crystalline state Ge atoms are in an octahedral configuration. Ga is four fold coordinated and the structure of GaSb is similar in both as-deposited and annealed samples. In their current form, our stacked phase change materials structures are not favorable to multistate storage. With further improvements in controlling the crystallization of individual layers, the stacked structures could achieve better characteristics than their single films counterparts. Further investigations in which a buffer conductive layer is inserted between the stacked films are envisaged.

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¹See <http://www.itrs.net> for International Technology Roadmap for Semiconductors, Emerging Research Devices (2012).

²G. I. Meijer, *Science* **319**(5870), 1625 (2008).

³M. Wuttig and N. Yamada, *Nature Mater.* **6**, 824 (2007).

⁴J. Kalb, M. Wuttig, and F. Spaepen, *J. Mater. Res.* **22**, 748 (2007).

⁵D. Lencer, M. Salinga, and M. Wuttig, *Adv. Mater.* **23**, 2030 (2011).

⁶J. Hegedus and S. R. Elliot, *Nature Mater.* **7**, 399 (2008).

⁷M. Popescu, F. Sava, A. Velea, and A. Lőrinczi, *J. Non-Cryst. Solids* **355**, 1820 (2009).

⁸A. Velea, *J. Non-Cryst. Solids* **357**, 2626 (2011).

- ⁹D. Loke, T. H. Lee, W. J. Wang, L. P. Shi, R. Zhao, Y. C. Yeo, T. C. Chong, and S. R. Elliott, *Science* **336**, 1566 (2012).
- ¹⁰G. Bruns, P. Merkelbach, C. Schlockermann, M. Salinga, M. Wuttig, T. D. Happ, J. B. Philipp, and M. Kund, *Appl. Phys. Lett.* **95**, 043108 (2009).
- ¹¹S. Raoux, A. K. König, H.-Y. Cheng, D. Garbin, R. W. Cheek, J. L. Jordan-Sweet, and M. Wuttig, *Phys. Status Solidi B* **249**, 1999 (2012).
- ¹²K. L. Chopra and S. K. Bahl, *J. Appl. Phys.* **40**, 4171 (1969).
- ¹³M. K. Santala, B. W. Reed, S. Raoux, T. Topuria, T. LaGrange, and G. H. Campbell, *Appl. Phys. Lett.* **102**, 174105 (2013).
- ¹⁴D. Lencer, M. Salinga, B. Grabowski, T. Hickel, J. Neugebauer, and M. Wuttig, *Nature Mater.* **7**, 972 (2008).
- ¹⁵T.-Y. Lee, K.-B. Kim, B.-K. Cheong, T. S. Lee, S. J. Park, K. S. Lee, W. M. Kim, and S. G. Kim, *Appl. Phys. Lett.* **80**, 3313 (2002).
- ¹⁶D. J. Gravesteyn, *Appl. Opt.* **27**, 736 (1988).
- ¹⁷T. Matsunaga, J. Akola, S. Kohara, T. Honma, K. Kobayashi, E. Ikenaga, R. O. Jones, N. Yamada, M. Takata, and R. Kojima, *Nature Mater.* **10**, 129 (2011).
- ¹⁸Y.-F. Lai, J. Feng, B.-W. Qiao, X.-G. Huang, Y.-F. Cai, Y.-Y. Lin, and T.-A. Tang, *Chin. Phys. Lett.* **23**, 2516 (2006).
- ¹⁹Y. Hu, M. Sun, S. Song, Z. Song, and J. Zhai, *Integrated Ferroelectr.* **140**, 8 (2012).
- ²⁰X. Zhou, L. Wu, Z. Song, F. Rao, K. Ren, C. Peng, S. Song, B. Liu, L. Xu, and S. Feng, *Appl. Phys. Lett.* **103**, 072114 (2013).
- ²¹N. Papandreou, H. Pozidis, T. Mittelholzer, G. F. Close, M. Breitwisch, C. Lam, and E. Eleftheriou, in *IEEE International Memory Workshop (IMW)* (2011).
- ²²F. Bai, H. Zhang, S. Gupta, and S. Kurinec, *Mater. Sci. Forum* **687**, 677 (2011).
- ²³A. Devasia, D. MacMahon, S. Raoux, K. A. Campbell, and S. K. Kurinec, *Thin Solid Films* **520**, 3931 (2012).
- ²⁴C.-F. Chen, A. Schrott, M. H. Lee, S. Raoux, Y. H. Shih, M. Breitwisch, F. H. Baumann, E. K. Lai, T. M. Shaw, P. Flaitz, R. Cheek, E. A. Joseph, S. H. Chen, B. Rajendran, H. L. Lung, and C. Lam, in *IEEE International Memory Workshop* (2009).
- ²⁵A. Velea, M. Popescu, A. Lőrinczi, F. Sava, I.-D. Simandan, and C. Mihai, *J. Optoelectron. Adv. Mater.* **13**, 1594 (2011).
- ²⁶S. Raoux, R. M. Shelby, J. Jordan-Sweet, B. Munoz, M. Salinga, Y.-C. Chen, Y.-H. Shih, E.-K. Lai, and M.-H. Lee, *Microelectron. Eng.* **85**, 2330 (2008).
- ²⁷L. van Pieterse, M. H. R. Lankhorst, M. van Schijndel, A. E. T. Kuiper, and J. H. J. Roosen, *J. Appl. Phys.* **97**, 083520 (2005).
- ²⁸M. N. Schneider, P. Urban, A. Leineweber, M. Döblinger, and O. Oeckler, *Phys. Rev. B* **81**, 184102 (2010).
- ²⁹M. Frumar, B. Frumarova, P. Nemecek, T. Wagner, J. Jedelsky, and M. Hrdlicka, *J. Non-Cryst. Solids* **352**, 544 (2006).
- ³⁰V. Nazabal, M. Cathelinaud, W. Shen, P. Nemecek, F. Charpentier, H. Lhermite, M. L. Anne, J. Capoulade, F. Grasset, A. Moreac, S. Inoue, M. Frumar, J. L. Adam, M. Lequime, and C. Amra, *Appl. Opt.* **47**, C114 (2008).
- ³¹P. Nemecek, M. Frumar, J. Jedelský, M. Jelínek, J. Lančok, and I. Gregora, *J. Non-Cryst. Solids* **299–302**, 1013 (2002).
- ³²M. J. Schoning, C. Schmidt, J. Schubert, W. Zander, S. Mesters, P. Kordos, H. Lutha, A. Leginc, B. Seleznev, and Y. G. Vlasov, *Sens. Actuators B* **68**, 254 (2000).
- ³³K. E. Youden, T. Grevatt, R. W. Eason, H. N. Rutt, R. S. Deol, and G. Wyllangowski, *Appl. Phys. Lett.* **63**, 1601 (1993).
- ³⁴M. Popescu, A. Velea, F. Sava, A. Lőrinczi, A. Tomescu, C. Simion, E. Matei, G. Socol, I. N. Mihailescu, A. Andronie, and I. Stamatina, *Phys. Status Solidi A* **207**, 516 (2010).
- ³⁵E. Morales-Sanchez, E. Prokhorov, J. Gonzalez-Hernandez, and A. Mendoza-Galvan, *Thin Solid Films* **471**, 243 (2005).
- ³⁶S. Raoux, J. L. Jordan-Sweet, and A. Kellock, *J. Appl. Phys.* **103**, 114310 (2008).
- ³⁷M. Chen, K. A. Rubin, and R. W. Barton, *Appl. Phys. Lett.* **49**, 502 (1986).
- ³⁸S. Raoux, H.-Y. Cheng, M. A. Caldwell, and H.-S. P. Wong, *Appl. Phys. Lett.* **95**, 071910 (2009).
- ³⁹I. Friedrich, V. Weidenhof, W. Njoroge, P. Franz, and M. Wuttig, *J. Appl. Phys.* **87**, 4130 (2000).
- ⁴⁰C. N. Borca, D. Grolimund, M. Willmann, B. Meyer, K. Jefimovs, J. Vila-Comamala, and C. David, *J. Phys.: Conf. Ser.* **186**, 012003 (2009).
- ⁴¹G. K. Williamson and W. H. Hall, *Acta. Metal.* **1**, 22 (1953).
- ⁴²See <http://xrdua.ua.ac.be/> for XRDUa, 2D Powder-XRD Analysis.
- ⁴³See <http://www.crystalimpact.com/match/> for Match! Phase Identification from Powder Diffraction.
- ⁴⁴B. Ravel and M. Newville, *J. Synchrotron Radiat.* **12**, 537 (2005).
- ⁴⁵Y. Maeda and M. Wakagi, *Jpn. J. Appl. Phys., Part 1* **30**, 101 (1991).
- ⁴⁶R. Mazelsky, M. S. Lubell, and W. E. Kramer, *J. Chem. Phys.* **37**, 45 (1962).
- ⁴⁷A. V. Kolobov, J. Tominaga, P. Fons, and T. Uruga, *Appl. Phys. Lett.* **82**, 382–384 (2003).
- ⁴⁸O. Uemura, Y. Sagara, M. Tsushima, T. Kamikawa, and T. Satow, *J. Non-Cryst. Solids* **33**, 71 (1979).
- ⁴⁹G. B. Fisher, J. Tauc, and Y. Verhelle, in *Amorphous and Liquid Semiconductors*, edited by J. Stuke (Taylor and Francis, London, 1974), p. 1259.
- ⁵⁰S. J. Pickart, Y. P. Sharma, and J. P. de Neufville, *J. Non-Cryst. Solids* **34**, 183 (1979).
- ⁵¹P. Boolchand, B. B. Triplett, S. S. Hanna, and J. P. de Neufville, *Mossbauer Effect Methodology* (Plenum, New York, 1974).
- ⁵²A. V. Kolobov, P. Fons, J. Tominaga, A. L. Ankudinov, S. N. Yannopoulos, and K. S. Andrikopoulos, *J. Phys.: Condens. Matter* **16**, S5103 (2004).
- ⁵³D. Ielmini and Y. Zhang, *Appl. Phys. Lett.* **90**, 192102 (2007).
- ⁵⁴S. K. Bahl and K. L. Chopra, *J. Appl. Phys.* **41**, 2196 (1970).
- ⁵⁵S. Raoux, H.-Y. Cheng, B. Muñoz, and J. Jordan-Sweet, in *Proceedings of the 8th Europ. Phase Change and Ovonic Sci. Symp. EPCOS* (2009).
- ⁵⁶A. V. Sapelkin, S. C. Bayliss, A. G. Lyapin, V. V. Brazhkin, and A. J. Dent, *Phys. Rev. B* **56**, 11531 (1997).
- ⁵⁷H. Y. Cheng, S. Raoux, and J. L. Jordan-Sweet, in *Proceedings of the 10th Europ. Phase Change and Ovonic Sci. Symp. EPCOS* (2011).
- ⁵⁸S. Raoux, C. Cabral, L. Krusin-Elbaum, J. L. Jordan-Sweet, K. Virwani, M. Hitzbleck, M. Salinga, A. Madan, and T. L. Pinto, *J. Appl. Phys.* **105**, 064918 (2009).
- ⁵⁹J. I. Langford, R. J. Cernik, and O. Louer, *J. Appl. Cryst.* **24**, 913 (1991).
- ⁶⁰M. Putero, M.-V. Coulet, T. Ouled-Khachroum, C. Muller, C. Baetz, and S. Raoux, *Appl. Phys. Lett.* **103**, 231912 (2013).
- ⁶¹N. Kaiser, *Thin Solid Films* **116**, 259 (1984).
- ⁶²M. Kaiser, L. van Pieterse, and M. A. Verheijen, *J. Appl. Phys.* **96**, 3193 (2004).
- ⁶³J. M. Del Pozo, M. P. Herrero, and L. Diaz, *J. Non-Cryst. Solids* **185**, 183 (1995).
- ⁶⁴Y. G. Choi, A. Kovalskiy, B.-K. Cheong, and H. Jain, *Chem. Phys. Lett.* **534**, 58 (2012).
- ⁶⁵T. Matsunaga, H. Morita, R. Kojima, N. Yamada, K. Kifune, Y. Kubota, Y. Tabata, J.-J. Kim, M. Kobata, E. Ikenaga, and K. Kobayashi, *J. Appl. Phys.* **103**, 093511 (2008).