The Crystallization Behavior of Ga-Sb Materials as a Function of Composition for Phase Change Random Access Memory

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ABSTRACT

The crystallization times, crystallization temperatures and crystallinity of Ga-Sb phase change materials with various Ga concentrations (13-50 at.%) were studied. All Ga-Sb materials we studied have higher crystallization temperatures, T_x, than $Ge_2Sb_2Te_5$, and the T_x increases significantly with increasing Ga concentration. An increase of crystallization time with increasing Sb content for as-deposited, amorphous films was observed. However, the trend is reversed for melt-quenched, amorphous films except for $Ga_{50}Sb_{50}$. The stoichiometric $Ga_{50}Sb_{50}$ and the material $Ga_{13}Sb_{87}$ show the shortest re-crystallization times. Ga-Sb material is a promising candidate for technological applications since it combines fast speed and high thermal stability.

Key words: Ga-Sb, phase transitions, crystallization time

1. INTRODUCTION

Phase change random access memory (PCRAM) is a promising candidate for next-generation nonvolatile memory technology due to its remarkable characteristics, such as high switching speed, long cycle life and good scalability. The most commonly used materials, $Ge_2Sb_2Te_5$, either doped or undoped, have proven adequate for NOR flash applications. However, for more stringent applications such as automotive and for DRAM-like performance, a material with short crystallization time (τ_x), high crystallization temperature (T_x) and large resistance switching window between the amorphous and crystalline states is desired.

Ga-Sb at a stoichiometric composition of Ga:Sb = 50:50 has a high melting temperature of 711.7 ^oC [1]. Consequently, a high crystallization temperature is expected for this composition. It crystallizes in the ZnS type face-centered cubic structure with a lattice constant a = 6.095 Å [2]. There is also a eutectic composition at Ga:Sb = 12 : 88 [1]. Because of good absorption at laser wavelengths used in CDs (780 nm), the first application of Ga-Sb was in 1987 [3-4] as a recording media for write-once optical storage which could only be programmed from the as-deposited, amorphous phase to the crystalline phase due to the limitation of the laser pulse width of the tester. Writing of amorphous marks in the crystalline material was not possible because of self-erasure. The available laser pulse was too long to enable melt-quenching due to the extremely fast re-crystallization of this material. Recently, it has been demonstrated that amorphization times of ~ 100 ps can be achieved using femtosecond laser pulse irradiation at moderate fluences for $Ge_2Sb_2Te_5$ [5]. With modern ultra-fast lasers melt-quenching of Ga-Sb materials is now possible and it would be very interesting to do further studies on their crystallization behavior for both as-deposited and melt-quenched, amorphous samples. It is known that the crystallization times for as-deposited, amorphous materials and melt-quenched, amorphous materials can be very different [6, 7] and the latter is the technologically most relevant.

Stoichiometric films of $Ga_{50}Sb_{50}$ were found to have very short (<15 ns) crystallization times for the transition from as-deposited, amorphous films to crystalline films [4]. Other compositions of Ga-Sb phase change material with Ga content ranging from 10 at. % to 17 at. % were proposed for high-speed optical media where the crystallization properties of these materials are very similar to doped Sb-Te materials [8]. It is believed that some of the fastest crystallizing phase change materials belong to doped Sb-Te materials, which are close in compositions to the eutectic point of the Sb-Te phase diagram [9, 10]. However, high-speed materials usually show low amorphous phase stability and high media noise [10]. On the contrary, the Ga-Sb materials are characterized by fast crystallization times, but have much better stability of the amorphous phase [10] resulting in phase change materials that combine high

crystallization rate and good thermal stability. However, the optimization of phase change materials is largely an empirical process. In this study, we investigated Ga-Sb materials with variable compositions and systematically explored their properties in terms of usefulness for PCRAM applications, including crystallization times (τ_x), crystallization temperatures (T_x), crystallinity and resistivity as a function of temperature (R vs. T).

2. EXPERIMENTS

The Ga-Sb films were prepared by co-sputtering from compound $Ga_{50}Sb_{50}$ and elemental Sb targets and the film composition was varied by controlling the relative power for the two sputtering sources. The films were 30 nm thick and the Ga fractions as determined by Rutherford Backscattering Spectrometry were 12.6, 18.8, 25.3, 34.9 and 51.9 at. % with an error of ± 0.5 at. %, as shown in detail in Table I. The substrates were Si wafers covered with a 30 nm Al_2O_3 thermal barrier layer for crystallization time measurements and a 1 μm thick SiO_2 films for resistivity vs. temperature measurements. Deposition was performed at room temperature and films were amorphous as deposited. Crystallization times were measured using a custom-made static laser tester [11]. Resistivity vs. temperature was measured using also a custom-made setup that contacted two large Al pads with a small gap deposited by thermal evaporation using a shadow mask. Measurements were performed in nitrogen at a heating rate of 1 ºC /s and during subsequent cool down.

Time-resolved x-ray diffraction (XRD) was used to study the crystallization behavior of these materials. Beamline X20C at the National Synchrotron Light Source has a sample chamber which contains a boron nitride heater to anneal samples in a purified helium atmosphere. The beamline is equipped with a high-throughput synthetic multilayer monochromator and the X-ray wavelength was 1.797 Å. A high photon mass density of about 10^{14} photons/cm/s was delivered by a high-throughput synthetic multilayer monochromator.

To measure crystallization time samples were exposed to laser pulses of various power and duration using a pulsed laser with a wavelength of 658 nm while film reflectivity was constantly monitored at the same location using a low power cw laser (probe laser, 635 nm). The beam profile at the sample was Gaussian with a diameter at 1/e = 1 μm. A single-pulse exposure for as-deposited amorphous films was used to determine the power and time needed for crystallization. The reflectivity vs. time recordings showed a reflectivity increase or decrease at the start of the laser pulse but this was reversed when the laser pulse was switched off before crystallization. Crystallization was indicated by a sudden increase in reflectivity that persisted after the end of the high power laser pulse. The $Ga_{50}Sb_{50}$ films are an exception where crystallization is accompanied by a decrease in reflectivity during the high power laser pulse. The phase transformation behavior can be deduced by plotting the change in reflectivity R (defined as $\Delta R/R=(R_{after}-R_{before})/R_{before}$ where R_{before} and R_{after} are the reflectivity before and after the single laser pulse, respectively) as a function of laser power and duration [12]. To measure the re-crystallization times of melt-quenched, amorphous material the samples were first heated to temperatures 30 ^{o}C above their respective crystallization temperatures for 10 min in a nitrogen atmosphere. A laser pulse with fixed duration and power was applied to produce a successful melt-quenched area in a crystalline film first. Then a second pulse with variable power and width at the same location was used to attempt the re-crystallization of the melt-quenched spots. A detailed description of the measurement procedures was reported in another paper [12].

3. RESULTS & DISCUSSION

Figure 1 shows the crystallization temperatures T_x as a function of composition in the Ga-Sb-Te ternary phase diagram. The T_x of the compositions of this study, as indicated from H to G in the ternary diagram, was determined by resistivity vs. temperature measurements, which are shown in Fig. 2. By raising the Ga content, the T_x of binary Ga-Sb films is increased and the stoichiometric composition GaSb (composition G) has the highest T_x. It is even higher than T_x of other Ga-Sb-Te alloys described in the literatures [13-15]. The films with 50 at.% Ga had the highest resistivity, and with 13 at.% Ga the lowest. At T_x the resistivity dropped sharply in one single step for all of the films we studied. Upon cooling the resistivity of the films remained low with weak temperature dependency except for stoichiometric films of $Ga_{50}Sb_{50}$, which exhibited a slight increase of resistivity upon cooling. The stoichiometric compound had the highest resistance at its crystalline state promising a benefit for reducing the reset current during the PCRAM cell operation. However, it had the lowest electrical contrast among the films. With increasing Sb content, up to four orders of magnitude electrical contrast is observed, but T_x also decreases. The materials with high Ga content promise

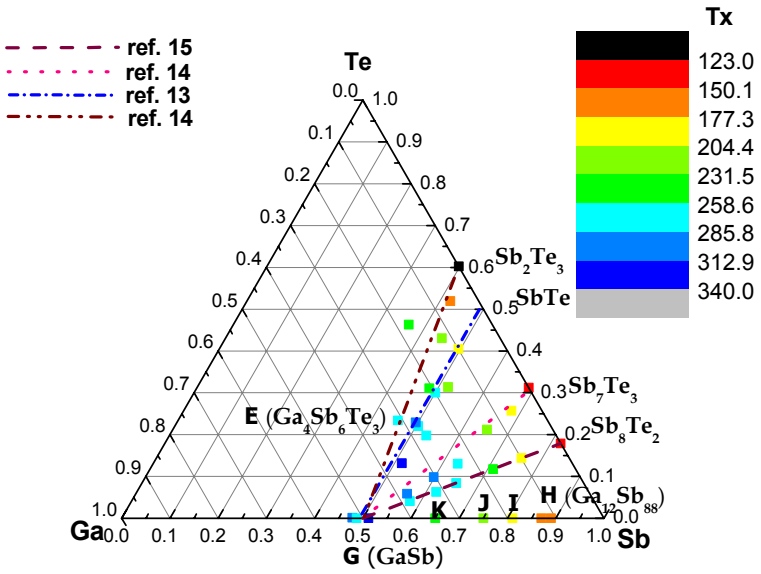

Fig. 1 Crystallization temperature T_x as a function of composition in the Ga-Sb-Te ternary phase diagram. Ga-Sb compositions in this study are marked as H to G.

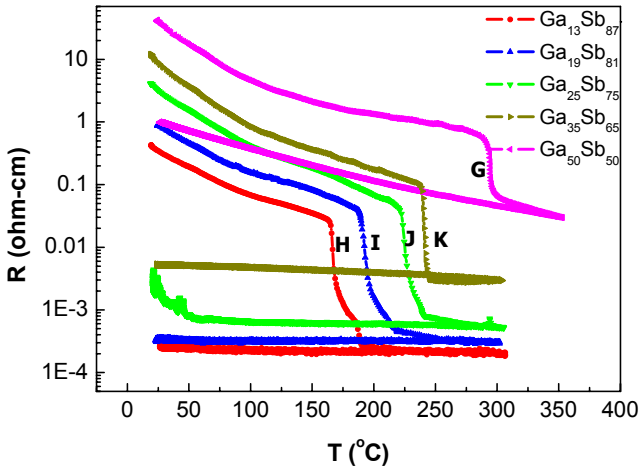

Fig. 2 Resistivity as a function of temperature for GaSb films of various Ga content during a heating ramp to 350 °C at 1 °C/s and subsequent cooling back to room temperature.

Table I Summary of crystallization temperatures T_x, crystallization speed τ_x for as-deposited and melt-quenched materials, electrical contrast and optical contrast for GaSb compositions. Ra and Rc are the resistivities in the amorphous phase before heating and in the crystalline phase after heating to 350 ºC, respectively, measured at room temperature.

Nominal fraction	Composition (at %)		T_x (°C) (From	T_x (°C) (From	τ_x	τ_x	Electrical contrast	Optical contrast
F_{nom},	Ga	Sb	R-T)	XRD)	(as-deposited)	(melt-quenched)	(Ra/Rc)	(ΔR/R)(%)
H	12.6	87.4	169	200	760	5	2.3×10^3	16.7
I	18.8	81.2	194	220	525	26	2.9×10^3	13.74
J	25.3	74.7	227	239	360	35	1.1×10^4	15.2
K	34.9	65.1	240	259	370	191	4.2×10^3	4.23
G	50	50	296	315	57	19	4.4×10^1	7.2

very good thermal stability because of their high T_x. Detailed compositions, the T_x and electrical contrast of studied materials are summarized in Table I.

Figures 3(a) and (b) show the relative change in reflectivity as a function of power and duration of an as-deposited-amorphous, and melt-quenched-amorphous stoichiometric $Ga_{50}Sb_{50}$ (composition G), respectively. Figures. 3(c) and (d) show the crystallization behavior of Ga-Sb with 12.6 at.% Ga (composition H), which is very close to the eutectic compositions with 12 at.% Ga, for an as-deposited-amorphous and melt-quenched-amorphous film, respectively. A decrease in reflectivity for crystallization (blue color) was found for stoichiometric $Ga_{50}Sb_{50}$, whereas an increase in reflectivity (red color) was observed for $Ga_{13}Sb_{87}$ (composition H) and the other Ga-Sb compositions we studied. It is known that most phase change materials, such as $Ge_2Sb_2Te_5$, exhibit an increase in reflectivity for crystallization, while they show a decrease in reflectivity for amorphization [16]. The $Ga_{50}Sb_{50}$ is an exception from the typical behavior. The reflectivity change upon the crystallization of binary Ga-Sb alloys exhibits an increase until the concentration of Ga is 44 at%. The melting temperature of Ga and Sb are 29.8 °C and 630.76 °C,

respectively, but congruent melting at a high temperature of 711.7 ^{o}C was found for the $Ga_{50}Sb_{50}$ compound [1], which is much higher than elemental Ga and Sb materials. Therefore, it is not surprising that $Ga_{50}Sb_{50}$ has unusual crystallization properties. In addition, stoichiometric $Ga_{50}Sb_{50}$ showed fast crystallization time for both as-deposited and melt-quenched samples. However, the $Ga_{13}Sb_{87}$ showed a very fast re-crystallization time for the melt-quenched-amorphous sample, even faster than 5 ns, and a much slower time in as-deposited-amorphous samples. It was reported that a long nucleation time (~4.5 μs) was required for as-deposited-amorphous $Ga_{15}Sb_{85}$ material, while a fast erasure time of 31 ns was measured for melt-quenched-amorphous films where a growth-dominated mechanism was suggested for this material [10]. Nucleation is not necessary for the re-crystallization of melt-quenched-amorphous samples and re-crystallization can proceed by fast crystal growth. Although we did not measure such long incubation time as described in the literature, crystallization time is not a fixed value for a given material and depends on the capping layer, the substrate, as well as the film thickness [12, 17]. Furthermore, for $Ga_{13}Sb_{87}$ the crystallization probability for a given laser power and duration is rather stochastic, this is the typical

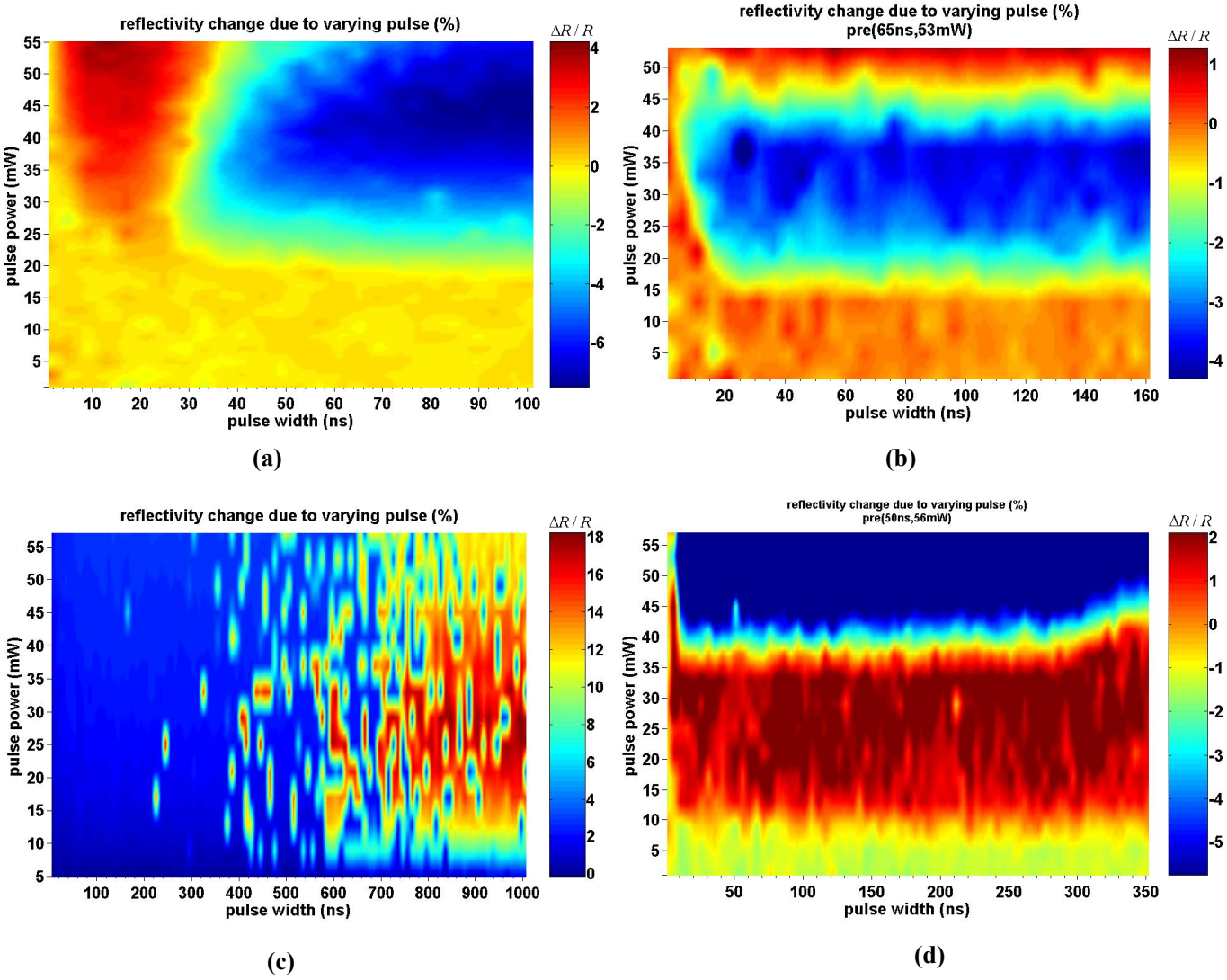

Fig. 3 (a)(b) Relative change in reflectivity as a function of pulse power and pulse width of stoichiometric $Ga_{50}Sb_{50}$ for as-deposited and melt-quenched, amorphous samples, respectively. (c)(d) Relative change in reflectivity of $Ga_{13}Sb_{87}$ for as-deposited and melt-quenched, amorphous samples, respectively.

behavior of a growth-dominated material with long incubation times and sparse nucleation events but fast crystal growth once nucleation has occurred [18]. The optical contrast of studied Ga-Sb films is also summarized in Table I. It was found that an increased reflectivity change occurred with Sb incorporation. It is known that a strong correlation exists between optical contrast and mass density changes for phase-change materials [19]. A high optical contrast (16.7 %) of the eutectic composition $Ga_{13}Sb_{87}$ (composition H) implies a large mass density change upon crystallization, which could possibly lead to void formation after back-end of line (BEOL) process of PCRAM fabrication.

Laser tester data were analyzed by plotting the relative change in reflectivity as a function of laser pulse length for the power where the fastest crystallization occurred, e.g. at 35 mW for Fig. 3(b). Figure 4 summarizes the crystallization times of both as-deposited, and melt-quenched-amorphous samples needed to complete 90 % of the phase transformation (90 % reflectivity change) as a function of Ga content. It can be seen that the crystallization times for as-deposited materials decrease with increasing Ga content, while a very different trend is observed for melt-quenched material. For higher Sb content longer incubation time is required suggesting a growth-dominated crystallization mechanism for Sb-rich Ga-Sb materials. On the contrary, fast re-crystallization times are exhibited for Ga-Sb with increasing Sb content, except for $Ga_{50}Sb_{50}$. The technologically relevant crystallization time however is the re-crystallization of melt-quenched materials since this is the process occurring for re-writable optical storage discs and PCRAM cells. The stoichiometric $Ga_{50}Sb_{50}$ and $Ga_{13}Sb_{87}$, which is close to the eutectic composition

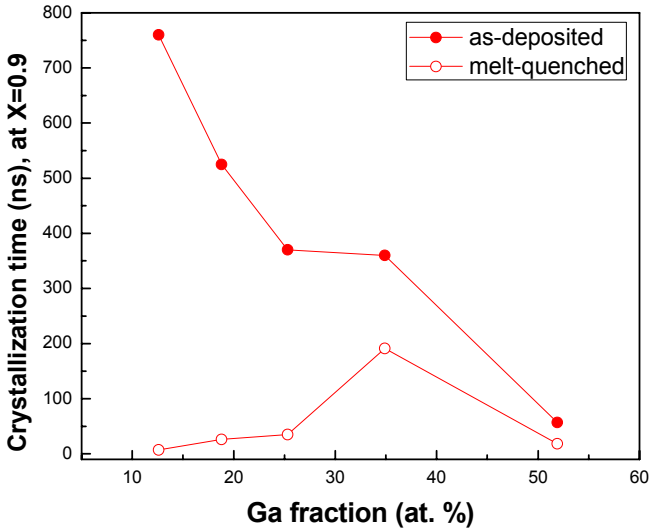

Fig. 4 Crystallization and re-crystallization times for a crystal fraction x of 0.9 as a function of Ga fraction of Ga-Sb materials in the as-deposited, amorphous and melt-quenched, amorphous states, respectively.

($Ga_{12}Sb_{88}$), show the fastest re-crystallization times. It is expected that Sb-rich compositions crystallize fast, similar to doped Sb-based compositions and doped Sb-Te, which have been shown to be fast growth (FG) materials [10]. However, the stoichiometric $Ga_{50}Sb_{50}$ shows surprisingly fast crystallization time comparable to Sb-rich Ga-Sb materials.

Time-resolved XRD revealed the crystallization behavior of these films as a function of composition. It confirmed that all as deposited films were amorphous. Figure 5 shows an example of the intensity of XRD peaks as a function of temperature for stoichiometric $Ga_{50}Sb_{50}$ and near-eutectic $Ga_{13}Sb_{87}$ films. The intensity of diffracted X-rays was recorded over a 2θ range of 15º using the diode-array detector centered at 31º during a heating ramp at 1 ºC/s to 450 ºC. At low temperature the films are amorphous and no XRD peaks are visible. XRD peaks appeared around 315 ºC for $Ga_{50}Sb_{50}$ and around 200 ºC for $Ga_{13}Sb_{87}$ films. θ-2θ scans acquired at room temperature after the ramps showed

the rhombohedral crystalline phase of Sb for the Sb-rich films with only strong (003) (see Fig. 5b) and (006) peaks. With increasing Ga content the spectra became more powder-like and remained in the Sb rhombohedral phase. For $Ga_{50}Sb_{50}$ the peaks could all be indexed to the cubic phase of $Ga_{50}Sb_{50}$ with a lattice constant of 6.09 Å which agrees well with the literature [2]. However, due to the similar characteristic XRD peaks of Sb and $Ga_{50}Sb_{50}$ it is difficult to distinguish between Sb and $Ga_{50}Sb_{50}$ peaks and it is difficult to determine whether the Ga-Sb materials crystallize in the rhombohedral Sb structure or in a combination of Sb and $Ga_{50}Sb50$ crystal phases. It has been reported that Sb-rich $Ga_{15}Sb_{85}$ in the bulk is not stable and will phase separate into $Ga_{50}Sb_{50}$ and Sb [20]. This does not necessarily have to be the case in thin films used for phase change recording media. The crystallization temperatures derived from XRD data are all higher than those from resistivity vs. temperature curves, which are shown in Fig. 2. The Ga-Sb

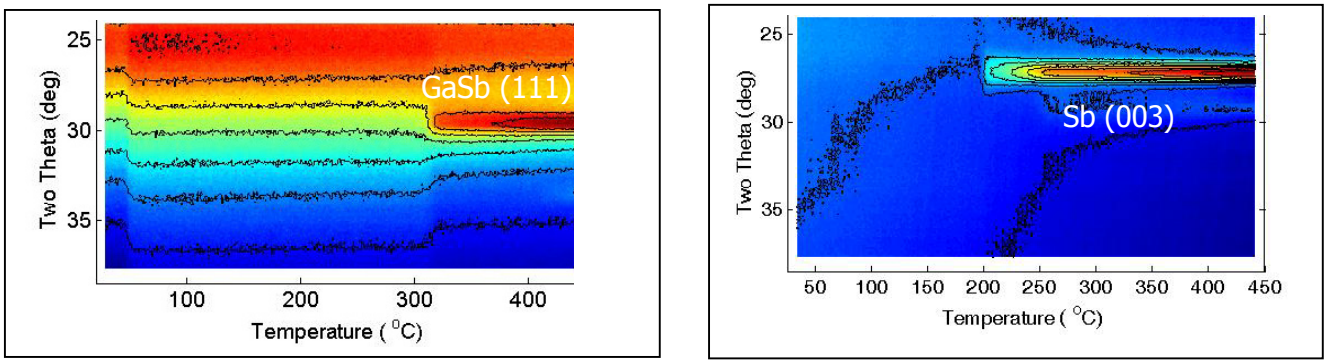

Fig. 5 (a) XRD peak intensity as a function of temperature T during heating at 1 ºC/s to 450 ºC of a stoichiometric GaSb film. (b) XRD peak intensity during heating at 1 ºC/s to 450 ºC of a film with 87.4 at% Sb.

films only show one phase transition from the amorphous phase to the rhombohedral phase for temperatures up to 450 ^{o}C, unlike $Ge_2Sb_2Te_5$ which crystallizes first in a rock-salt, metastable crystalline phase and at higher temperature transforms into a hexagonal, stable crystalline phase. All of the films have very high T_x, compared to $Ge_2Sb_2Te_5$ (~150 ^{o}C) indicating potentially better data retention for PCRAM.

4. CONCLUSIONS

This study opens a new possibility for a promising candidates for phase-change memory materials. The stoichiometric $Ga_{50}Sb_{50}$ material and the $Ga_{13}Sb_{87}$ material (very close to the eutectic composition) show the fastest crystallization speed among the films we studied. The former also has the highest T_x, highest resistivity, but with low resistance contrast; the latter has lower T_x and resistivity, but the resistance contrast is much higher. The trade-off needs to be made when choosing the optimum composition for a given application. The fast re-crystallization time and much better thermal stability are encouraging but attention will need to be paid to possible phase segregation for these new materials, especially for off-stoichiometric alloys.

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Simone Raoux is a Research Staff Member at the IBM T. J. Watson Research Center. She received her MS degree in 1984 and Ph.D. degree in physics in 1988 both from Humboldt University, Berlin, Germany. From 1988 to 1991 she worked as a Staff Scientist at the Institute for Electron Physics in Berlin, Germany, doing research in the field of electrical breakdown. From 1992 to 2000, she was a Staff Scientist at Lawrence Berkeley National Laboratory and performed research in the fields of vacuum arc deposition, ion implantation, photoemission electron microscopy, X-ray magnetic circular dichroism, and near-edge X-ray absorption fine structure spectroscopy. She joined IBM in 2000 and her current research interests include the physics and materials science of phase change materials.

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