

Crystallization properties of Ga-Sb phase change alloys

Simone Raoux^{1,2}, Huai-Yu Cheng^{1,3}, Jean Jordan-Sweet², Thomas Monin⁴, Feng Xiong^{2,5,6},
Anja König⁷, Daniele Garbin⁸, Roger Cheek^{1,2}, Eric Pop^{5,6}, and Matthias Wuttig^{7,9}

¹IBM/Macronix PCRAM Joint Project

²IBM T. J. Watson Research Center, P. O. Box 218, Yorktown Heights, NY, USA

³Macronix International Co., Ltd., Emerging Central Lab., 16 Li-Hsin Rd., Science Park, Hsinchu, Taiwan, ROC

⁴Grenoble National Institute of Technology, Phelma Minatec, Grenoble, France

⁵Department of Electrical and Computer Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

⁶Now at Department of Electrical Engineering, Stanford University, Stanford, CA 94305, USA

⁷Institute of Physics (IA) – RWTH Aachen University, D-52056 Aachen, Germany

⁸Turin Polytechnic University, Dipartimento di Elettronica, 24 C.so Duca degli Abruzzi, Turin, Italy

⁹JARA – Fundamentals of Information Technology, RWTH Aachen University

Contact author: simoner@us.ibm.com

ABSTRACT

Ga-Sb alloys are potential candidates for Phase Change Random Access Memory (PCRAM) applications. Ga-Sb alloys of variable compositions including the stoichiometric GaSb and several Sb-rich compositions were studied using static laser testing and time-resolved X-ray diffraction. It was found that the stoichiometric alloy has an unusual inverse optical contrast compared to typical phase change materials as the crystalline phase has lower reflectivity than the amorphous phase. Slightly Sb-rich alloys show decrease in reflectivity upon crystallization at lower temperature but increase in reflectivity at higher temperature which are related to GaSb crystallization and subsequent Sb segregation, respectively. Very Sb-rich materials exhibit positive optical contrast only, similar to conventional phase change materials.

Key words: Ga-Sb, static laser testing, time-resolved X-ray diffraction, optical contrast

1. INTRODUCTION

Phase Change Random Access Memory (PCRAM) is an emerging technology that potentially could replace several established memory technologies such as flash or DRAM with very application specific requirements, or it could serve as a storage class memory with more universal properties. The phase change materials are at the core of PCRAM technology development and much research is devoted to design and optimize phase change materials for specific applications.

Ga-Sb alloys have been studied as possible phase change materials for PCRAM because they show high thermal stability of the amorphous phase, high crystallization temperatures, and fast switching [1-3]. They have been investigated for phase-change optical storage [4], and PCRAM devices have been demonstrated as well [5]. Density-functional simulations of as-deposited and melt-quenched stoichiometric GaSb and eutectic GaSb₇ alloys also indicate their interesting properties [6].

In the present study we systematically investigated the changes in crystallization properties of stoichiometric and Sb-rich Ga-Sb alloys using static laser testing and time-resolved X-ray diffraction.

2. EXPERIMENTS

Ga-Sb thin films of variable composition were deposited from a nominally stoichiometric GaSb target and an elemental Sb target by co-sputtering at a pressure of 0.27 Pa in 46 sccm Argon flow. Depositions were done at room temperature and as deposited films were amorphous. The film thickness was approximately 50 nm and the substrates included 30 nm SiO₂ on Si for static laser

testing and 500 nm SiO₂ on Si for time-resolved X-Ray Diffraction (XRD) measurements. Sample composition was determined by Rutherford Backscattering Spectrometry (RBS).

Static laser testing measurements used a custom-made laser tester with a high-power diode laser (pump laser) at a wavelength of 658 nm to heat the sample, and a highly attenuated cw HeNe laser (read laser, 633 nm) to constantly monitor the sample reflectance. The change in reflectance $\Delta R/R$ was determined by measuring the reflectance before the pump laser pulse (R_{before}), after the pump laser pulse (R_{after}), and normalizing the difference to R_{before} so that $\Delta R/R = (R_{\text{after}} - R_{\text{before}})/R_{\text{before}}$. Time-resolved XRD was performed at beamline X20C of the National Synchrotron Light Source at Brookhaven National Laboratory. The setup is equipped with a boron nitride heater in a helium atmosphere and a high-throughput synthetic multilayer monochromator set for an X-ray wavelength of 1.797 Å. The intensity of the diffracted X-ray peaks was measured at a ramp rate of 3 °C/s from room temperature to 600 °C. A fast linear diode array detector was centered at $2\theta = 31^\circ$ so that the intensity of diffracted X-ray peaks in the angular range of $2\theta = 23.5 - 38.5^\circ$ was detected.

3. RESULTS & DISCUSSION

Ga-Sb films were deposited with nominal compositions between 50 and 92 at. % Sb including one alloy with 88 at. % Sb which is the eutectic composition. Table I summarizes the nominal compositions and the RBS data. It can be seen that the nominally stoichiometric sample is slightly Sb rich. In the remainder of the paper we will refer to the samples with their nominal composition.

Table I: Nominal and measured by RBS compositions of the samples studied here.

Nominal composition Ga:Sb in at. %	RBS data	
	Ga (± 0.5 at. %)	Sb (± 0.5 at. %)
50:50	44.7	55.3
30:70	30.3	69.7
20:80	24.0	76.0
12:88	13.3	86.7
8:92	9.1	90.9

Crystallization times as function of sample composition were studied using the static laser tester. Figure 1 (a-e) plots the change in reflectance as a function of laser power and duration for amorphous, as-deposited samples exposed to an array of pump laser pulses. As observed already in [1, 2], Ga:Sb=50:50 shows an unusual optical contrast because the crystalline phase has a lower reflectance than the amorphous phase (Fig.1(a)). Almost all other phase change materials we have studied so far have a higher reflectance in the crystalline phase [7]. For the alloy with intermediate composition (30:70) two levels of reflectance in the crystalline state are observed (Fig. 1(b)), at low pulsed laser power (corresponding to a lower temperature) the reflectance is reduced upon crystallization, and for higher laser power (corresponding to higher temperature) the reflectance in the crystalline state is higher than in the as-deposited, amorphous phase, confirming previous results on an alloy with similar composition Ga:Sb=36:64 [2]. The Sb-rich alloys with an Sb-fraction of 76 at. % and more behave like conventional phase change materials with a positive optical contrast (Fig.1(c-e)). The eutectic material is very different as it has a much longer crystallization time compared to all other compositions (Fig. 1(d)). It also shows a stochastic crystallization probability for very similar pulse laser powers and durations in the region of marginal crystallization. This is the typical behavior of a growth dominated phase change material with sparse nucleation events but fast crystal growth [7]. All other compositions exhibit very reproducible crystallization probability for similar pulse laser powers and duration which is the typical behavior for nucleation dominated phase change materials with many nucleation sites within the laser spot and relatively slow crystal growth. Fig. 1 (f) shows that the stoichiometric composition (50:50) has the shortest crystallization time of about 40 ns.

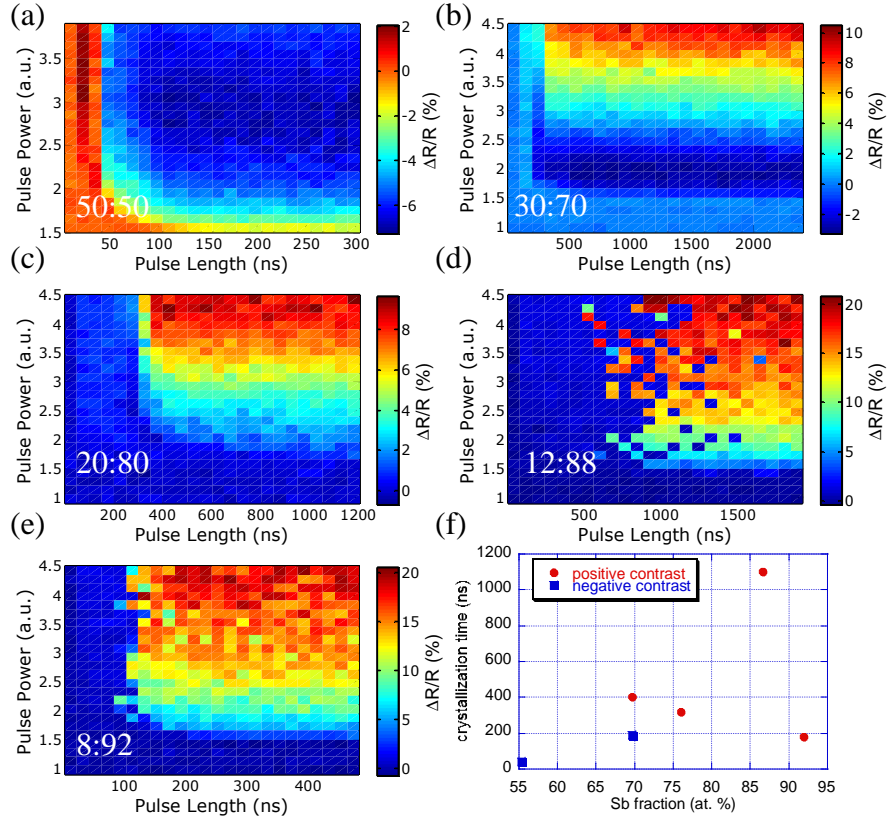


Figure 1: (a-e) Change in reflectance of various Ga-Sb alloys as a function of pulse laser power and duration. (f) Crystallization time as a function of Sb fraction.

From a technological standpoint the crystallization times of as-deposited phase change materials are irrelevant because in optical disks and PCRAM devices melt-quenched, amorphous material is present, in most cases bordering crystalline material. Under these circumstances crystallization times can sometimes be orders of magnitude different, typically faster and thus beneficial for optical storage and PCRAM [7]. On the other hand, crystallization temperatures of the melt-quenched, amorphous phase are often substantially reduced [8], and retention data collected on actual PCRAM device can be much worse than predicted from retention data measured on as-deposited, amorphous films [9]. We therefore measured re-crystallization times of melt-quenched, amorphous materials as well. This was done in the following way. First a crystalline area was produced by scanning the pulse laser over the sample surface. A dual pulse experiment was then performed where first identical pulses produced melt-quenched, amorphous marks in the crystalline area, and second pulses in the same location but with variable power and duration attempted re-crystallization of the melt-quenched marks. Figure 2 summarizes the results. For the Ga:Sb=50:50 sample the crystalline area was darker than the as-deposited, amorphous film. The melt-quenched, amorphous marks were again as bright as the as-deposited, amorphous film, and re-crystallization led to a negative contrast (Fig. 2(a), similar to the first crystallization of as-deposited, amorphous film with a single laser pulse.

We attempted in two ways to create large area material in the lowest reflectance phase for the Ga:Sb=30:70 alloy by either scanning the pulse laser over the sample or by furnace annealing just above the crystallization temperature, but without success. It is possible that this phase can only be created when the sample temperature is elevated for a very short time as it is in the pulse laser experiment. By laser scanning and furnace annealing the resulting material had always the reflectance of the brightest material in Fig. 1(b), therefore the re-crystallization also shows only positive contrast as indicated in Fig. 2(b). Fig. 2(c) demonstrates a very fast re-crystallization, and comparing Figs. 1(f)

and 2(d) confirms that crystallization times of as-deposited, amorphous and melt-quenched, amorphous material surrounded by crystalline material can be very different. Even the trend with Sb fraction is very different. We also produced crystalline Ga:Sb=12:88 and 8:92, but were unable to create melt-quenched marks. This is possibly due to the fact that these materials exhibit such a fast re-crystallization that the material re-crystallizes during cooling after the laser pulse. The thermal time constant of the phase change film on top of the 30 nm SiO₂ on Si can be estimated from finite element calculations and is on the order of 5-10 ns [10]. If the trend for the re-crystallization times continues and they are further reduced with increasing Sb content this might well be the case.

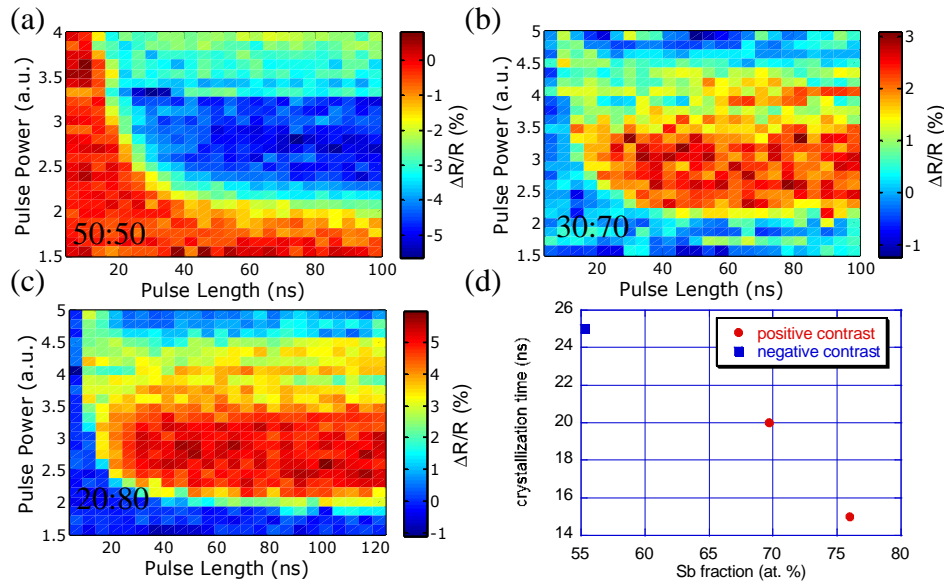


Figure 2: (a-c) Change in reflectance of various Ga-Sb alloys as a function of pulsed laser power and duration in a re-crystallization experiment. (d) Re-crystallization time as a function of Sb fraction.

Time-resolved XRD revealed details of the crystallization process (Fig. 3). With increasing Sb fraction X-ray peaks appear at lower temperatures indicating a lower crystallization temperature for Sb-rich compositions, in good agreement with previous results [2]. The Ga:Sb=50:50 composition exhibited exclusively cubic GaSb peaks. With increasing Sb content also rhombohedral Sb peaks appeared, first at higher temperature for the 30:70 sample, then at the same temperature as the GaSb peaks as Sb content is further increased. This allows to explain the three different levels of brightness for the 30:70 sample. As deposited material is amorphous leading to an intermediate brightness. When GaSb crystallizes the sample has a negative contrast and becomes darker. When finally at higher temperature the Sb also crystallizes the net effect of negative weak GaSb contrast and positive strong Sb contrast is a positive contrast. Figure 4 depicts the temperatures at which the GaSb and Sb peaks appear, and Fig. 5 shows the theta-2theta XRD spectra which were acquired at room temperature after the heating ramps from Fig. 3. The 8:92 composition has the same rhombohedral structure and high degree of texture as we have observed previously for pure Sb films sputtered under similar conditions.

4. CONCLUSION

Phase change alloys based on the Ga-Sb material system exhibit phase transition properties and optical contrast which depends on the material composition. This offers an opportunity to tailor them for specific PCRAM applications. The stoichiometric composition is characterized by an unusual negative optical contrast, and slightly Sb-rich alloys can even show three levels of brightness which we identified using XRD as: darkest – GaSb crystalline and Sb amorphous, intermediate level – GaSb and Sb amorphous, and brightest – GaSb and Sb crystalline.

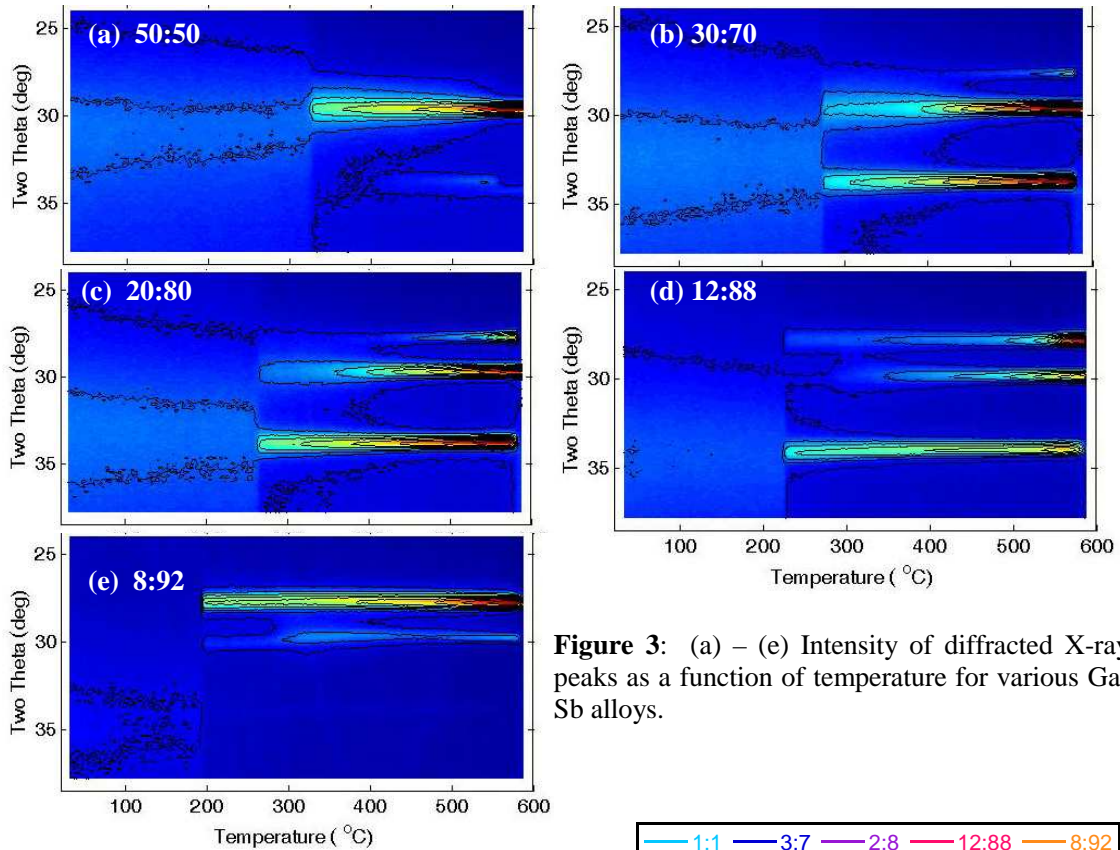


Figure 3: (a) – (e) Intensity of diffracted X-ray peaks as a function of temperature for various GaSb alloys.

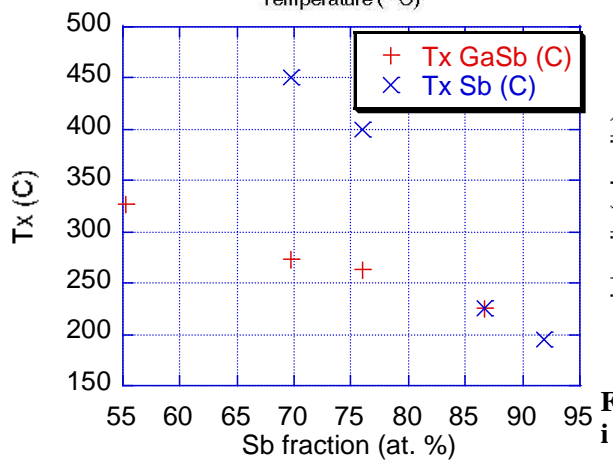


Figure 4: Temperature T_x at which GaSb and Sb peaks appear as function of the Sb fraction.

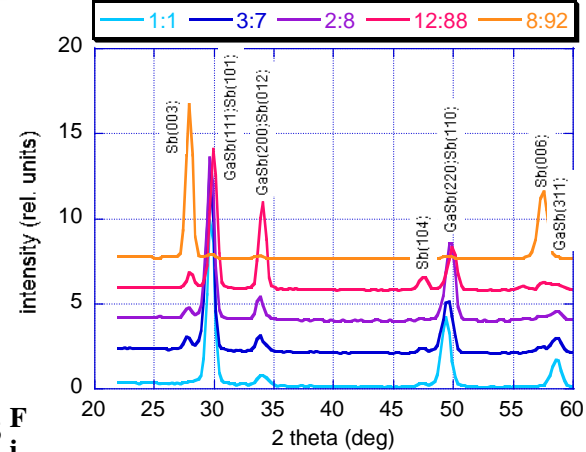


Figure 5: Theta-2theta XRD scans after ramps to 600 °C.

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Biographies

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 at the Institute for Electron Physics in Berlin, Germany and from 1992 to 2000 at LBNL, Berkeley. She joined IBM in 2000 and her current research interests include the physics and materials science of phase-change materials.

Huai-Yu Cheng is a Senior Researcher at Macronix Emerging Central Lab. She received her B.S. degree (2001), M.S. (2003) and Ph.D. degree (2007) in Materials Science and Engineering from National Tsing Hua University, Hsinchu, Taiwan. In 2007, she joined Macronix in the Advanced Memory R&D. Since 2008 she has been member in the IBM/Macronix PCRAM Joint Project and assigned first to the IBM Almaden Research Center, later at the IBM T. J. Watson Research Center. Her current research interest is the development of advanced phase-change materials.

Jean Jordan-Sweet is a Research Staff Member at the IBM T. J. Watson Research Center. Her research interests include phase transitions, metal/polymer interface structure, advanced high-k gate dielectric thin film structure, metal silicides, diffusion barrier failure, thin silicon-oxide film interface structure, defect structure in strain-relieved SiGe films, stability of strained-silicon CMOS structures, and micro-diffraction of interfacial strain and defects.

Thomas Monin received his B.S. in Physics in 2011 and is currently completing his Master's Degree in Nanotechnology from the Grenoble National Institute of Technology. He is doing his master thesis at IBM T.J. Watson on phase change materials and their application in memory devices.

Feng Xiong is a Ph.D. candidate in electrical engineering at the University of Illinois at Urbana-Champaign. He is currently an intern at IBM T. J. Watson Research Center studying phase change materials.

Anja König graduated from RWTH Aachen University, Germany, with a M.S. degree in physics in 2010 and an M.B.A in 2011. After interning at the IBM T. J. Watson Research Center in 2012 she is now project coordinator for new battery technologies at Robert Bosch GmbH.

Daniele Garbin received his M.Sc. degree in Micro and Nano Technologies for Integrated Systems in 2012 from Politecnico di Torino, EPFL Lausanne and Grenoble INP. He is currently a Ph.D. student at CEA-Leti, France, where he is conducting research on novel nonvolatile memory technologies.

Roger Cheek received his Ph.D. in chemistry from the University of North Texas in 1994. He joined IBM's Microelectronics Division in 1994. He moved to IBM's Research Division in 2004 to work on phase-change memory.

Eric Pop received his M.Eng./B.S. in EE and B.S. in Physics from MIT (1999) and his Ph.D. in EE from Stanford (2005). Between 2005-2007 he worked at Intel, and did post-doctoral work at Stanford. He joined the ECE faculty at UIUC in 2007 and received tenure in 2012. He joined Stanford faculty in 2013 and is now a professor in the EE department. His interests are in energy efficient electronics.

Matthias Wuttig received his diploma from Cologne (1986) and Ph.D. from Aachen University (1988). He has been a Full Professor of Physics at RWTH Aachen since 1997 and presently serves as Speaker of the Strategy Board of the university. His main scientific interest is the development of novel materials.