

Effect of Ion Implantation on Crystallization Properties of Phase Change Materials

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ABSTRACT

Ion implantation has been used to re-amorphize crystalline phase change material $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST) close to room temperature and without melting. Germanium and carbon ions were used at energies ranging from 2 KeV to 120 KeV and doses ranging from $8 \times 10^{12} \text{ cm}^{-2}$ to $3 \times 10^{15} \text{ cm}^{-2}$. The GST films were between 15 and 90 nm thick, and were annealed before implantation to transform them into the rocksalt crystalline phase. It was observed that a relatively low minimum dose was sufficient to amorphize the GST. Re-amorphized films showed increased crystallization temperature, in particular for high implanted doses. This effect was more pronounced for C ion implantation. High-dose implanted samples have properties similar to as-deposited material while low-dose implanted samples behave more like melt-quenched material in terms of crystallization times. Ion implantation also leads to a small increase in the mass density of as-deposited, amorphous films from 5.5 to 5.72 g/cm^3 . For films deposited at 200 °C which are in the rocksalt crystalline phase the mass density is higher (6.02 g/cm^3). It is only very slightly modified by ion implantation even though the ion implantation re-amorphizes the material. The differences in crystallization times and temperatures for the various amorphous films show again that amorphous material properties depend strongly on the way they were produced and treated.

Key words: $\text{Ge}_2\text{Sb}_2\text{Te}_5$, ion implantation, amorphization, crystallization temperatures, crystallization times

1. INTRODUCTION

Phase change materials exist in an amorphous phase and in a crystalline phase which have distinctly different physical properties such as optical reflectivity and electrical resistivity. Precisely these differences are used to store information in phase-change-based re-writable optical storage and phase change memory (PCM). To switch from the amorphous state to the crystalline state the material is heated above the crystallization temperature for a time that is sufficiently long for crystallization. The switch from the crystalline to the amorphous state is reached by melting and rapidly quenching the material in technological applications such as optical storage discs or PCM devices. It has been found however that ion implantation can also be applied to re-amorphize crystalline phase change materials [1, 2]. Even though there is currently no technological application that utilizes this amorphization method it still allows to produce amorphous films of various properties and to study their crystallization behavior. It has been shown that amorphous phase change materials can have very different properties depending on the way they were produced (for example by deposition at room temperature, by melt-quenching, or ion implantation) or treated (for example by heating to temperatures below the crystallization temperature or by ion bombardment) [3, 4]. Here we report on a study of ion

implantation into crystalline phase change material $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST) to re-amorphize it without melting but close to room temperature and over large area. We show that amorphous GST of various properties such as crystallization temperature, crystallization time, or mass density can be produced by ion implantation.

2. EXPERIMENTS

Thin films of the phase change material $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST) were deposited by magnetron sputter deposition from an alloy target and in most cases capped *in situ* with a thin (5-10 nm) SiO_2 layer to prevent oxidation. The film composition was determined by a combination of Rutherford backscattering spectrometry (Ge to Sb+Te ratio) and particle-induced x-ray emission (Sb to Te ratio), and was found to be Ge = 28.6 ± 0.5 at. %, Sb = 25.7 ± 5 at. % and Te = 45.7 ± 5 at. %. The measurement errors are relatively large for the Sb to Te ratio because of the very similar masses, but the alloy appears to be slightly Te poor compared to the stoichiometric composition of 2:2:5. The GST films were between 15 and 90 nm thick, and were annealed at 200 °C in N_2 for a minimum time of 90 s to transform them into the rocksalt crystalline phase. X-ray diffraction (XRD) confirmed that these annealing conditions transformed the as-deposited amorphous films into the rocksalt phase. Other samples were deposited at 200 °C and XRD also indicated that these samples were as-deposited in the rocksalt phase.

Ion implantation was performed using a Varian ion implanter E220HP. Low ion current densities (232 nA/cm^2) were selected to avoid self-annealing and the sample temperature was close to room temperature during implantation. Ge and C ions were implanted with ion energies ranging from 2 KeV to 120 KeV depending on the ion species, sample thickness and intended projected range. Implantation doses ranged from $8 \times 10^{12} \text{ cm}^{-2}$ to $3 \times 10^{15} \text{ cm}^{-2}$. For very thick samples (60 and 90 nm) multiple implantations at various energies were performed to amorphize the whole film thickness.

Time-resolved XRD was performed at beamline X20C of the National Synchrotron Light Source at Brookhaven National Laboratory. The XRD endstation is equipped with a BN heater capable of heating samples in a purified He atmosphere at rates up to 27 K/s and to temperatures up to 1000 °C. A fast linear diode array detector recorded the intensity of the diffracted XRD peaks over a 2θ range of 15 ° and was placed at the 2θ angle that contains XRD peaks of interest. The x-ray wavelength used was 1.797 Å and measurements were typically performed with the center of the detector at $2\theta = 31$ ° so that the rocksalt (111) and (200) as well as the hexagonal (102) peaks could be detected.

Cross-sectional transmission electron microscopy (TEM) samples were prepared by a single-beam focused ion beam (FIB). For milling a 30 KeV Ga ions was used, followed by a low energy (10 KeV) beam for surface cleaning. The samples were capped with a protective 300 nm thick evaporated Al film to avoid amorphization by the FIB ion beam. Samples were then imaged in a FEI CM-12 TEM using bright field and micro-diffraction techniques to highlight layer crystallinity. TEM also showed partial amorphization of the underlying crystalline silicon substrate as shown in the images.

A static laser tester [5] was applied to measure crystallization times of as-deposited amorphous, melt-quenched amorphous and ion-implanted amorphous GST. Thin films of as-deposited amorphize and ion-implanted amorphize GST were exposed to laser pulses of variable power and duration using a high power pulsed laser with a wavelength of 658 nm while a low power cw laser (635 nm) monitored the reflectivity of the film before, during and after the high power laser pulse at the same location. Crystallization was indicated by an increase in reflectivity. To measure crystallization times of melt-quenched amorphize GST melt-quenched marks were first produced in a crystalline GST film using laser pulses of sufficient power and time to produce these marks without ablating the film. The melt-quenched amorphous marks were then attempted to re-crystallize using laser pulses of variable power and duration.

X-ray reflectivity (XRR) was used to measure film thickness and density. XRR data were collected on a Bruker high-resolution X-ray diffractometer with a monochromatic Cu K radiation source. Data were collected from 600 to 12,000 arcsec in step sizes of 20 arcsec with a count time of 5 s, and simulated using commercially available software. Even though these films were uncapped, a top native oxide layer grows on it. Thus, a top oxide layer, and an oxide interface layer (to account for the native oxide) were added to the layered structure model to fit the

data. Density and thickness of the layers were obtained from the best fits. The error in the thickness and density measurements was about 5 %.

3. RESULTS & DISCUSSION

It was found that crystalline GST films can be re-amorphized by ion implantation using Ge or C ions. When ion dose, ion energy and GST film thickness were varied it was observed that there is a minimum dose required that leads to amorphization as judged from XRD. This minimum dose depends on the ion species, ion energy and GST film thickness. For example, a 16 nm thick GST films can be re-amorphized using 30 KeV Ge ions for doses higher than $4 \times 10^{13} \text{ cm}^{-2}$. Figure 1 illustrates this example.

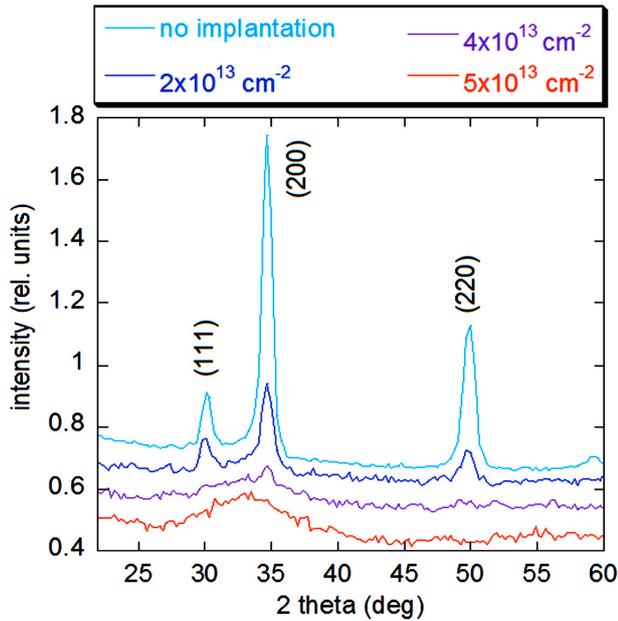


Figure 1: θ - 2θ scans of 16 nm GST film after annealing without ion implantation and after annealing and subsequent Ge ion implantation at an ion energy of 30 KeV and different doses. The unimplanted film is clearly crystalline in the rocksalt phase. A dose of $2 \times 10^{13} \text{ cm}^{-2}$ reduces the XRD peak intensity substantially. At a dose of $4 \times 10^{13} \text{ cm}^{-2}$ the film is almost completely amorphized, and for higher doses no XRD peaks are visible anymore.

Above this critical dose the films are amorphous after implantation as judged from x-ray diffraction. These films can be re-crystallized by heating. The heating was performed at the XRD beamline using a heating rate of 1 K/s. Figure 2 compares the time-resolved XRD data of as deposited amorphous and Ge ion-implanted amorphous GST.

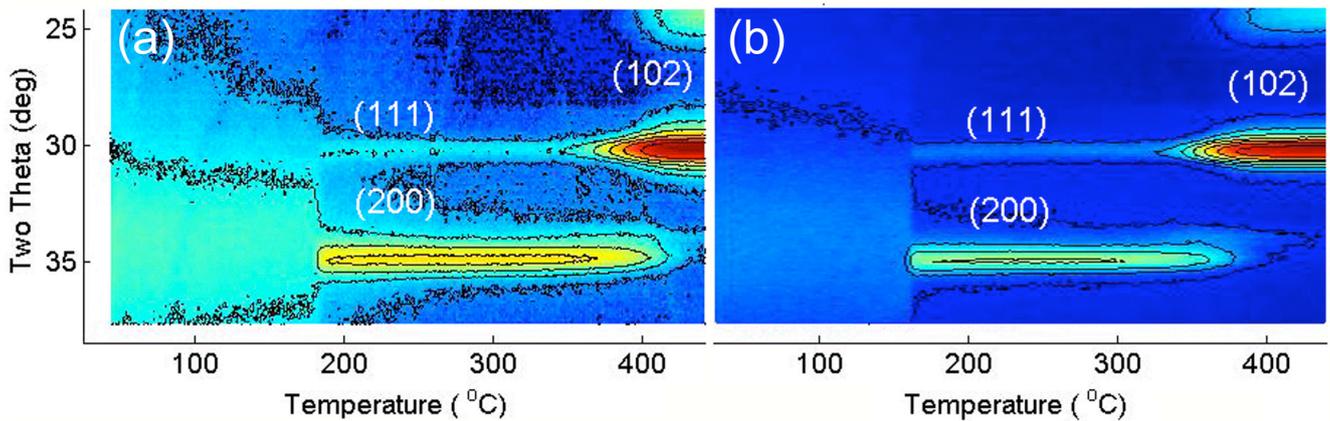


Figure 2: Intensity of diffracted XRD peaks as a function of temperature during a 1 K/s ramp for 16 nm thick GST sample (a) annealed at 200 °C for 90 s and subsequently amorphized by 30 KeV Ge ion implantation at a dose of 10^{15} cm^{-2} and (b) as-deposited-amorphous sample.

Low dose implanted samples show a re-crystallization temperature similar to as-deposited amorphous samples, but for higher doses the re-crystallization temperature is increased. For Ge ions of an energy of 30 KeV implanted into 16 nm GST the highest re-crystallization temperature was observed at a dose of 10^{15} cm^{-2} (the highest Ge ion dose used in this study) and it was 184 °C compared to 160 °C for as deposited amorphous GST (see Fig. 2). For C ion implantation this effect was even stronger. Figure 3 shows time-resolved XRD data for a 15 nm GST film implanted with C ions at an energy of 4 KeV and a dose of $3 \times 10^{15} \text{ cm}^{-2}$. Here we observed much increased crystallization temperatures (230 °C) and also much increased transition temperature from the rocksalt to the hexagonal phase compared to as deposited films (Fig. 2b).

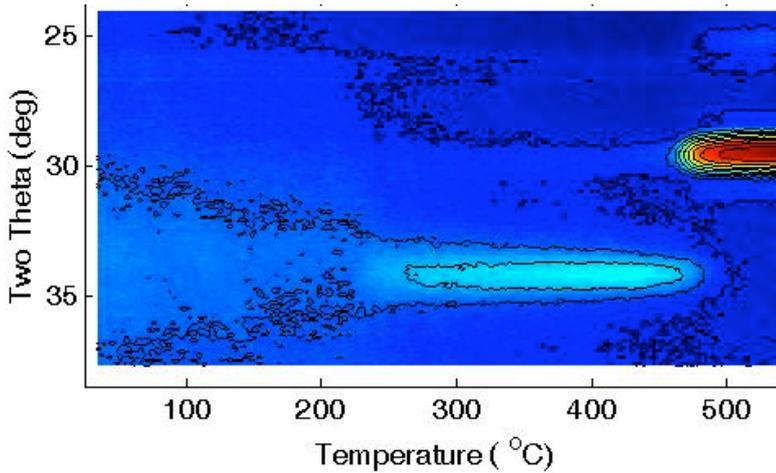


Figure 3: Time-resolved XRD data for a 15 nm GST film implanted with C ions at an energy of 4 KeV and a dose of $3 \times 10^{15} \text{ cm}^{-2}$. The re-crystallization temperature is greatly increased to 230 °C compared to as-deposited amorphous GST (see Fig. 2b).

Cross-sectional TEM confirms the crystalline nature of GST films after annealing and when implanted with doses below the critical dose as determined by XRD. The TEM image also confirms that GST films implanted with higher doses than the critical dose are amorphous (Fig. 4).

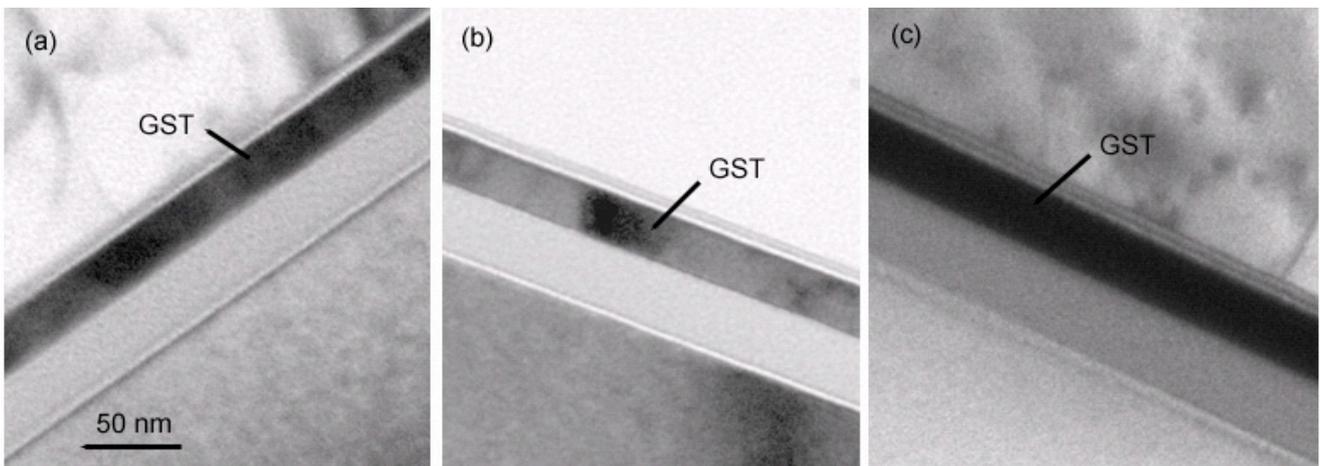


Figure 4: Cross-sectional TEM of 10 nm SiO_2 capping layer / 30 nm GST / 30 nm Al_2O_3 / Si. The very top layer is Al used for TEM sample preparation. (a) Sample deposited at room temperature and annealed at 200 °C for 90 s. GST shows crystallites. (b) Sample deposited at room temperature and annealed at 200 °C for 90 s, subsequently Ge ion implanted (30 KeV) at a dose of $2 \times 10^{13} \text{ cm}^{-2}$, below the critical dose for amorphization.

Some crystallites are still visible. (c) Sample deposited at room temperature and annealed at 200 °C for 90 s, subsequently Ge ion implanted (30 KeV) at a dose of $5 \times 10^{14} \text{ cm}^{-2}$, well above the critical dose for amorphization. The GST layer appears completely featureless.

Even thick GST films can be successfully amorphized by ion implantation using several different ion energies. Figure 5 shows the θ - 2θ scan of a 90 nm GST film deposited at room temperature, annealed at 200 °C for 90 s, and subsequently implanted by Ge ions at a dose of 10^{15} cm^{-2} each at energies of 30, 80 and 120 KeV. This film is clearly amorphous.

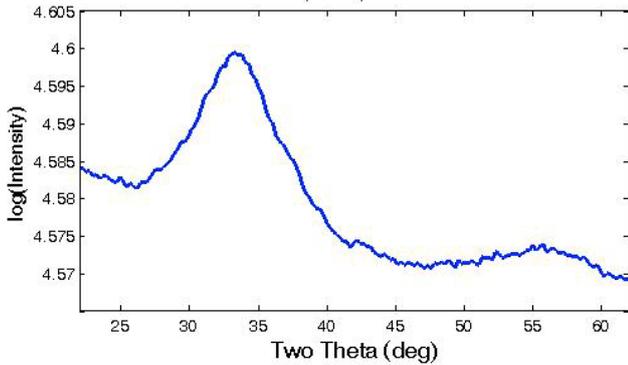


Figure 5: θ - 2θ scan of a 90 nm thick GST film deposited at room temperature, annealed at 200 °C for 90 s, and subsequently implanted by Ge ions at a dose of 10^{15} cm^{-2} each at energies of 30, 80 and 120 KeV. These energies correspond to projected Ge ion ranges of 20, 43 and 71 nm, respectively, as simulated by SRIM [6]. This film is clearly amorphous.

Laser testing was used to measure crystallization times of two implanted GST samples (Figures 6 and 7).

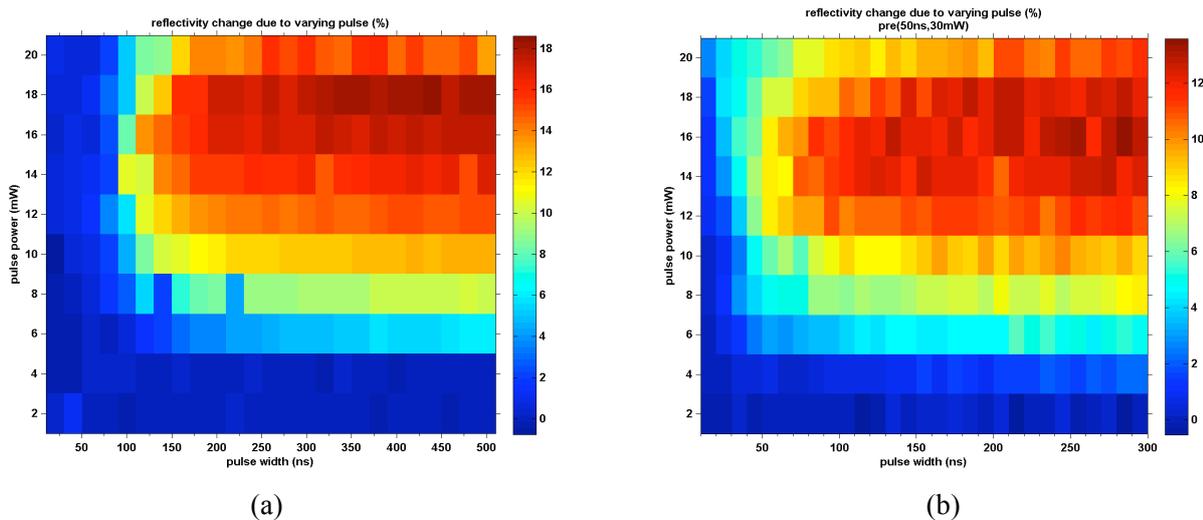


Figure 6: Change in reflectivity as a function of pulsed laser duration and power measured for 16 nm GST on 30 nm Al_2O_3 , capped with 5 nm SiO_2 . (a) as-deposited amorphous GST, (b) melt-quenched amorphous where the melt-quenched mark was produced by a 50 ns, 30 mW pre-pulse.

It is known that as-deposited and melt-quenched GST have different crystallization times [7]. This can be seen in Fig. 6a and Fig. 6b, as-deposited GST crystallizes in about 100 ns at the optimum laser power of about 16 mW while melt-quenched GST crystallizes faster in about 50 ns. The low dose implanted sample, Fig. 7a, has similar crystallization time to melt-quenched amorphous material, while the high-dose implanted sample, Fig. 7(b) has the longest crystallization times, slightly longer than as-deposited amorphous GST. It is not clear why the low-dose implanted GST, Fig. 7(a), needs higher laser power for crystallization than the other samples. All samples stem from the same wafer and were deposited at the same time. The crystallization of phase change materials is typically initiated by heterogeneous nucleation preferentially at surfaces and interfaces [8].

Since the ion implantation will modify the interfaces, both the interfaces to the capping layer and to the substrate by causing some intermixing, it is not surprising that crystallization times can be modified by ion implantation.

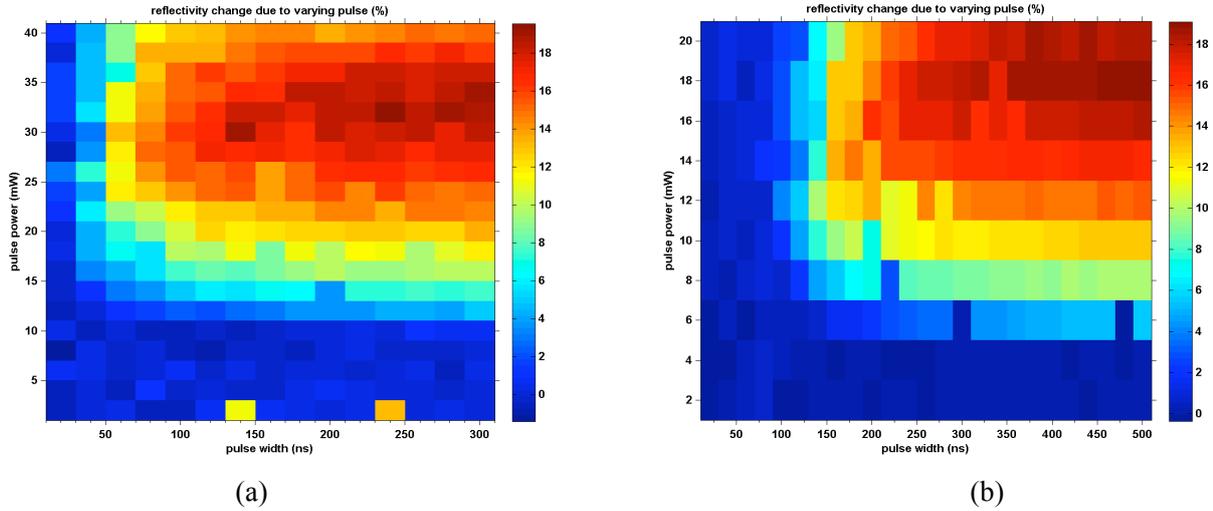


Figure 7: Change in reflectivity as a function of pulsed laser duration and power measured for 16 nm GST on 30 nm Al₂O₃, capped with 5 nm SiO₂. (a) crystallized and re-amorphized by Ge ion implantation (30 KeV) at a dose of $5 \times 10^{13} \text{ cm}^{-2}$ which is just above the amorphization threshold dose, (b) crystallized and re-amorphized by Ge ion implantation (30 KeV) at a dose of 10^{15} cm^{-2} well above the critical dose.

In addition we speculated that the crystallization time is faster for low-dose ion implantation since the amorphized material probably still contains small but separated crystallites that can be used to initiate nucleation. The higher the dose the fewer of these crystallites are present in the film.

It has been reported in the literature that ion implantation can densify phase change materials [9]. We performed a systematic study of the mass density of GST deposited either at room temperature or at 200 °C and treated in various ways by annealing and/or ion implantation. The samples were uncapped nominally 30 nm thick GST film deposited on Si, the actual film thicknesses were between 28 nm for the as deposited at room temperature sample to 20 nm for the sample deposited at 200 °C. For the XRR modeling an additional thin SiO₂ layer at the interface and a thin GeO_x layer at the surface were required for a good fit of the data. The final state of the GST films (amorphous or crystalline) was confirmed by XRD. The mass density was determined by a combination of x-ray reflectivity measurements, Rutherford backscattering spectroscopy, and particle-induced x-ray emission. Table I summarizes the results.

The mass densities for as deposited GST agree reasonably well with literature, 5.87 and 6.27 g/cm³ for the amorphous and crystalline phases, respectively [10]. We also find that ion implantation densifies films. What is particularly interesting is that we can produce amorphous films of substantially higher mass density than as deposited amorphous films.

Deposited at	Treatment	Final state	Mass density (g/cm ³)
Room temperature	none	amorphous	5.50
Room temperature	Ion implanted	amorphous	5.72
Room temperature	Annealed, ion implanted	amorphous	5.83
Room temperature	Annealed, ion implanted, annealed again	crystalline	5.97
200 °C	none	crystalline	6.02
200 °C	Ion implanted	amorphous	6.00
200 °C	Ion implanted, annealed	crystalline	6.08

Table I: Mass density of GST films deposited at different temperature and treated with different annealing and implantation steps. The annealing was done at 200 °C for 90 s, the ion implantation was performed using Ge ions at an energy of 30 KeV and a dose of 10^{15} cm⁻².

4. CONCLUSION

These experiments demonstrate again that the properties of amorphous phase change materials depend strongly on the way the amorphous state was produced and the way samples were treated. We found that Ge and C ion implantation pushes up the crystallization temperature by 24 °C for Ge and 60 °C for carbon when a dose of 10^{15} Ge/cm² and 3×10^{15} C/cm² is used. We also demonstrated that ion implantation of amorphous GST lead to increase in it the material density by 4 % for as-deposited amorphous GST. Even though all these films appear amorphous as judged from XRD their local order will be modified by ion implantation. It has been demonstrated that amorphous materials produced and treated in different ways can all appear amorphous when characterized XRD but can have a very different local order [3] and this degree of medium range local order influences their phase change properties.

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REFERENCES

1. A. M. Mio, E. Carria, R. De Bastiani, M. Miritello, C. Bongiorno, G. D'Arrigo, C. Spinella, M. G. Grimaldi, and E. Rimini, "Crystallization of ion amorphized Ge₂Sb₂Te₅ in nano-structured thin films", Mater. Res. Soc. Proc. Vol. 1251 (2010) 1251-H02-03
2. S. Raoux, G. M. Cohen, R. M. Shelby, H.-Y. Cheng, and J. L. Jordan-Sweet, "Amorphization of crystalline phase change material by ion implantation", Mater. Res. Soc. Proc. Vol. 1251 (2010) 1251-H02-06
3. B.-S. Lee, G. W. Burr, R. M. Shelby, S. Raoux, C. T. Rettner, S. N. Bogle, K. Darmawikarta, S. G. Bishop, and J. R. Abelson, "Direct observation of the role of supercritical nuclei in crystallization of a glassy solid," Science **326** (2009) 980
4. R. De Bastiani, A. M. Piro, M. G. Grimaldi, E. Rimini, G. A. Baratta, and G. Strazzulla, "Ion irradiation-induced local structural changes in amorphous Ge₂Sb₂Te₅ thin films," Appl. Phys. Lett. **92** (2008) 241925
5. M. Salinga, "Phase change materials for non-volatile electronic memories", PhD thesis, Technical University RWTH Aachen, Germany, 2008
6. J. F. Ziegler, J. P. Biersack, and U. Littmark, *The Stopping and the Range of Ions in Solids*, Pergamon, New York, 1985.
7. S. Raoux, R. Shelby, B. Munoz, M. Hitzbleck, D. Krebs, M. Salinga, M. Woda, M. Austgen, K.-M. Chung, and M. Wuttig, "Crystallization times of as-deposited and melt-quenched amorphous phase change materials," Europ. Phase Change and Ovonic Science Symp., Prague, Czech Republic, September 2008
8. J. Kalb, "Crystallization kinetics," in *Phase Change Materials: Science and Technology*, S. Raoux and M. Wuttig, Eds., Springer, 2009, pp. 125-148
9. E. Rimini, R. De Bastiani, E. Carria, M. G. Grimaldi, G. Nicotra, C. Bongiorno, and C. Spinella, "Crystallization of sputtered-deposited and ion implanted amorphous Ge₂Sb₂Te₅ thin films," J. Appl. Phys. **105** (2009) 123502
10. M. Wuttig, R. Detemple, I. Friedrich, W. Njoroge, I. Thomas, V. Weidenhof, H.-W. Wöltgens, and S. Ziegler, "The quest for fast phase change materials," J. Magn. Magnet. Mater. **249** (2002) 492

Biographies

Simone Raoux is a Research Staff Member at the IBM T. J. Watson Research Center. She received her M.S. degree (1984) and Ph.D. degree (1988) in physics 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. Since 2000 she has been with IBM. Her current research interests include the physics and materials science of phase change materials.

Guy M. Cohen received the B.Sc. degree in electrical engineering from Technion – Israel Institute of Technology, Israel in 1988, a M.Sc. degree in physical electronics from Tel-Aviv University in 1993, and a Ph.D. in electrical engineering from Technion – Israel Institute of Technology, Israel in 1998. His Ph.D. research included the study of tunnel devices and FETs made with InP/InGaAsP and related alloys for analog applications. In 1996 he was a visiting scholar with CNET, France-Telecom labs, Bangneux, France, where he studied the amphoteric carbon doping of InGaAsP layers matched to InP. Since 1998 he has been with IBM T.J. Watson Research Center in Yorktown Heights, NY where he had worked on topics such as self aligned double-gate MOSFETs, silicide for thin SOI, compliant substrates, strained-silicon-on-silicon and mixed orientation substrates. More recently, his research has focused on the study of silicon nanowires for CMOS technology.

Robert M. Shelby received his PhD from the University of California in 1978 and his BS from California Institute of Technology in 1972, both in Chemistry. He has been a Research Staff Member at IBM Almaden since 1979. His research has included nonlinear laser spectroscopy of defects in solids, frequency-domain data storage, the generation of squeezed light, optical quantum nondemolition measurement, squeezed optical solitons, and holographic data storage. Recently, he has worked on the characterization and study of phase change materials for nonvolatile solid state memory. He is a Fellow of the Optical Society of America.

Huai-Yu Cheng 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 for a researcher position in the Advanced Memory R&D Department focusing on the topic of phase change memory. Since 2008, she has been a research team member in the IBM/Macronix PCRAM Joint Project and assigned to the IBM T. J. Watson Research Center for the development of advanced phase-change materials.

Anita Madan received a PhD degree in Physics/Materials Science from Northwestern University in 1997. She then worked as a Research Scientist in the Advanced Coating Technology Group, affiliated with Northwestern University, designing and fabricating thin films for optical and hard coating applications. Since 2001, she has been working in the IBM Microelectronics Division as a member of the Failure Analysis Characterization team. She has been engaged in failure root cause analysis and supporting development of novel materials and processes for advanced microelectronic applications. At IBM, she has introduced non-destructive X-ray techniques to determine strain on reference pads and measure density of thin films.

John A. Ott received his Bachelor of Science in Electrical Engineering, Cum Laude from Fairleigh Dickenson University in 1988. He subsequently joined the IBM Thomas J. Watson Research Center in 1989. He did extensive TEM and SEM characterization work of SiGe thin films and devices for the development of IC manufacturing processes and aided in the design and implementation of UHV analysis system for a UHV-TEM. In 1992, he joined Steven's Institute of Technology as Facility Manager for the Advanced Technology Center. His projects included industrial and academic research, such as the development of holography on the Philips CM20-FEG, HR-TEM of nano-crystalline thin films and polymer studies. He also taught TEM, SEM and specimen preparation laboratory courses. He returned to IBM Thomas J. Watson Research Center in 1995, as a Process development engineer and is working on next generation device materials. His current interests are graphene synthesis, thin film growth, transmission electron microscopy and atomic force microscopy.

Jean Jordan-Sweet is a Research Staff Member in the Silicon Technology Department of IBM's T. J. Watson Research Center. She is responsible for the management and operation of three x-ray beamlines at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL), which are owned jointly by IBM and the NSLS. She has been an active member of the synchrotron community for 25 years. Research contributions have been made in the areas of two-dimensional phase transitions, metal/polymer interface structure, advanced high-k gate dielectric thin film structure, structural transformations in metal silicides and phase change materials, diffusion barrier failure, thin silicon-oxide film interface structure, defect structure in strain-relieved SiGe films, stability of strained-silicon CMOS structures, and microdiffraction of interfacial strain and defects.