Influence of Dopants on the Crystallization Temperature, Crystal Structure, Resistance, and Threshold Field for $Ge_2Sb_2Te_5$ and GeTe Phase Change Materials

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ABSTRACT

The phase change materials $Ge_2Sb_2Te_5$ (GST) and GeTe have been studied extensively for their application in re-writable optical storage and in phase change random access memory (PCRAM). We have investigated the influence of various dopants on the crystallization behavior and electrical switching properties of GST and GeTe. The dopants included nitrogen, silicon, titanium, and aluminum oxide. Time-resolved x-ray diffraction (XRD) showed that all GST samples (undoped and doped) first crystallized into the rocksalt crystal structure, and at higher temperature into the hexagonal phase. The crystallization temperature increased with doping, and also the transition temperature from the rocksalt crystal structure to the hexagonal crystal structure. For doped GeTe the crystal structure after heating was rhombohedral, similar to undoped GeTe, with slightly changed lattice constants. For GST, nitrogen doping was most efficient in terms of increased crystallization temperature. Ti-doped GeTe material had the highest crystallization temperature of around 350 ºC. Resistivity vs. temperature measurements revealed that most dopants lead to an increase in the resistivities of the amorphous phase with the exception of Ti. In the crystalline phase all dopants increased the resistivity for GST while they have little influence for GeTe. The crystallization temperatures measured by XRD and resistive vs. temperature measurements agreed within a few degrees. Measurements of the threshold field indicated that doping can also be used to tune this phase change material property. In particular doping with aluminum oxide for GST and nitrogen for GeTe leads to a substantial increase in threshold field which is desirable for ultra-scaled PCRAM devices.

Key words: phase change materials, doping, crystallization properties, threshold field

1. INTRODUCTION

The phase change materials $Ge_2Sb_2Te_5$ (GST) and GeTe are among the most commonly applied materials for phase change random access memory (PCRAM). PCRAM is a promising candidate for next-generation nonvolatile memory technology because of the fast switching times, high cycle numbers, good data retention and excellent scalability. For several applications, however, the properties of the phase change material limit the PCRAM device performance. For example, data retention is insufficient for automotive applications where data need to be retained at 150 ºC for over 10 years. It has been shown by several groups that doping can be an efficient way to modify the properties of phase change materials, and several dopants such as nitrogen [1], oxygen [1], silicon [2], silicon oxide [3], vanadium [4], titanium [4], silver [5], bismuth [6], or tin [7] have been proposed and described in the literature. *Ab initio* calculations also confirm that doping can influence the properties of both amorphous and crystalline phase change materials [8]. Several important material parameters can be improved for PCRAM applications. It is desirable to have materials with higher crystallization temperature because it can be expected that they show improved data retention.

In addition, increased resistance in both phases, in particular in the crystalline phase, will lead to reduced programming currents and reduced programming power. The threshold field is another important parameter that needs to be increased for ultra-scaled devices. In current PCRAM technology threshold voltages are on the order of 1 V, but these will be reduced with the device dimensions, and for very small devices the threshold voltage will become comparable to the reading voltage, which will disturb the device state by the reading operation. Materials with increased threshold fields are therefore required.

In this paper we investigate the influence of nitrogen, silicon, titanium, and aluminum oxide doping on the crystallization characteristics of GST and GeTe phase change materials. We study how crystallization behavior, crystallization temperatures, resistances and threshold field are modified by doping. Future studies should include the measurement of the crystallization time because it has been found also to be affected by doping [9] and it is another very important materials parameter as it determined the data rate.

2. EXPERIMENTS

Films were co-sputter deposited from GST and GeTe alloy targets, and silicon, titanium or aluminum oxide targets. For nitrogen doping, films were deposited from GST and GeTe alloy targets in an argon-nitrogen gas mixture. The substrates were Si wafers coated with 500 nm SiO_2 for XRD and resistivity vs. temperature measurement, the thickness of the phase change material films was 50 nm. Film composition was determined by Rutherford backscattering spectroscopy (RBS) and particle-induced x-ray emission (PIXE). Typical dopant concentrations were in the few per cent range. Table I summarizes the film compositions.

Phase change material	Dopant	Composition (at. %)
GST	None	Ge 23.3 Sb 27.3 Te 49.4
GST	N	Ge 21.0 Sb 246 Te 44.5 N 9.9
GST	Si	Ge 22.6 Sb 26.5 Te 47.9 Si 3.0
GST	Ti	Ge 22.0 Sb 25.8 Te 46.7 Ti 5.5
GST	Al_2O_3	Ge 22.4 Sb 26.2 Te 47.5 Al 0.4 O 3.5
GeTe	None	Ge 50.7 Te 49.3
GeTe	N	Ge 45.5 Te 44.2 N 10.3
GeTe	Si	Ge 48.7 Te 47.4 Si 3.9
GeTe	Ti	Ge 45.0 Te 43.8 Ti 11.2
GeTe	Al_2O_3	Ge 46.7 Te 45.5 Al 0.8 O 7.0

Table I: Composition of films used in this study. Composition was measured by a combination of RBS and PIXE. The accuracy of the Ge, (Sb+Te), N, Si, Ti, Al and O fraction is ± 0.5 at. %, the accuracy of the Sb to Te ratio is ± 5 at. % because Sb and Te are very close in mass density and difficult to distinguish by PIXE.

Thin films were characterized by *in situ* time-resolved x-ray diffraction (XRD). The measurements were performed during rapid thermal annealing in a purified helium atmosphere at beamline X20C of the National Synchrotron Light Source. The beamline is equipped with an *in situ* boron nitride heater stage and the intensity of the XRD peaks was detected by a fast linear diode array detector that monitors the intensity of the XRD peaks over a 2θ range of 15º. The center of the detector was located at 2θ = 31º which allowed the detection of strong GST and GeTe XRD peaks at the x-ray wavelength used of 1.797 Å.

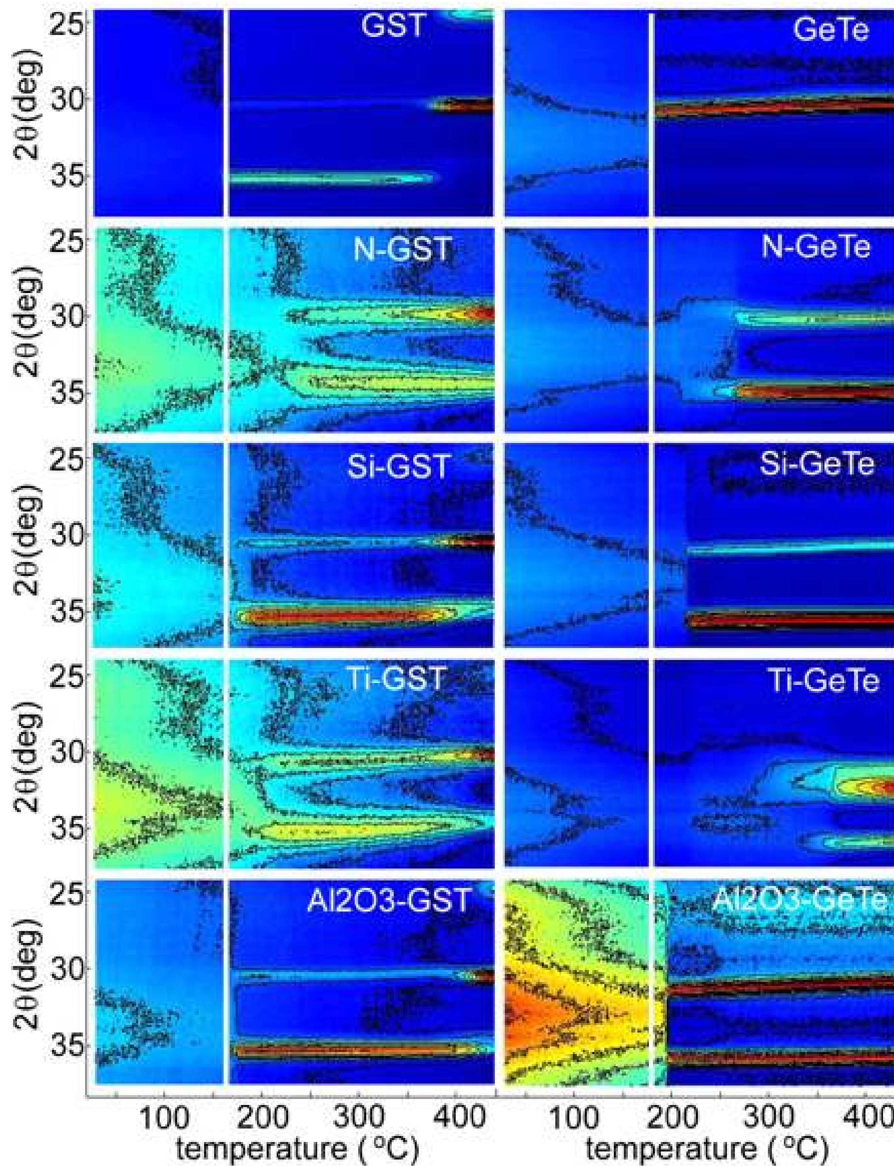
Resistivity vs. temperature was measured in a custom-made set-up in nitrogen atmosphere. A boron nitride heater was used to ramp the thin film samples at a rate of 5 ºC/min to a maximum temperature of 400 ºC. The measurements were performed in a van der Pauw configuration.

PCRAM devices were fabricated with the doped GST and GeTe materials as the storage material, and electrical testing of the devices was applied to determine the threshold fields. The devices were fabricated by optical lithography using tantalum bottom electrodes and aluminum top electrodes. Low-temperature lithographic processes were developed and implemented such that the phase change material was still in the amorphous, as-deposited state after device fabrication. Single cell devices of 1 μm^2 area were electrically tested by passing a 0-50 µA current sweep and recording the threshold voltage using a parameter analyzer. SET and RESET resistances were read at a voltage of

0.2V across the cell. The phase change material film thickness was 50 nm and the threshold fields were calculated from the threshold voltages assuming that the full 50 nm film thickness was amorphous. Threshold field measurements were performed on as fabricated cells where this assumption is justified.

3. RESULTS & DISCUSSION

Time-resolved x-ray diffraction revealed that all the dopants lead to an increase in the crystallization temperature. The most efficient dopant for increased crystallization temperature was nitrogen for GST and titanium for GeTe phase change material. Figure 1 shows the intensity of diffracted XRD peaks as a function of temperature for undoped and doped GST and GeTe, acquired at a ramp at 1 ºC/s to 450 ºC.



The material with the highest crystallization temperature was Ti doped GeTe, with a crystallization temperature around 350 ºC compared to undoped GeTe with a crystallization temperature around 170 ºC. The least effect had the Al_2O_3 doping, probably because of the low doping level. All GST samples (undoped and doped) first crystallized into the rocksalt crystal structure and at higher temperature into the hexagonal phase. Not only the crystallization temperature increased with doping, but also the transition temperature from the rocksalt crystal structure to the hexagonal crystal structure, up to 540 ºC for nitrogen-doped GST compared to 380 ºC for undoped GST. Doping also caused some transitions to be more gradual, in particular for N-GST and Ti-GST. For doped GeTe the crystal structure after heating was rhombohedral, similar to undoped GeTe with slightly changed lattice constants. Change in texture indicated by the change in relative peak intensity was observed as well.

Figure 1: Time-resolved XRD measurements on undoped and doped GST (left) and undoped and doped GeTe (right). Plotted is the intensity of diffracted XRD peaks as a function of temperature for a ramp at 1 ºC/s to 450 ºC.

The θ-2θ scans of undoped and doped GST and GeTe after a ramp to 450 ºC are depicted in Figures 2 and 3. The GST films are hexagonal with the exception of N-GST which is still in the rocksalt phase. Ramps to higher temperature confirmed that N-GST eventually also transitions to the hexagonal phase around 540 ºC.

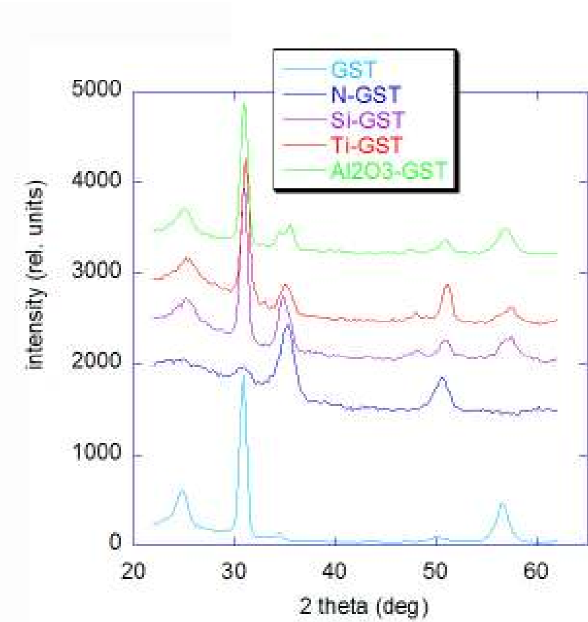


Figure 2: θ-2θ scans of undoped and doped GST after a ramp to 450 ºC.

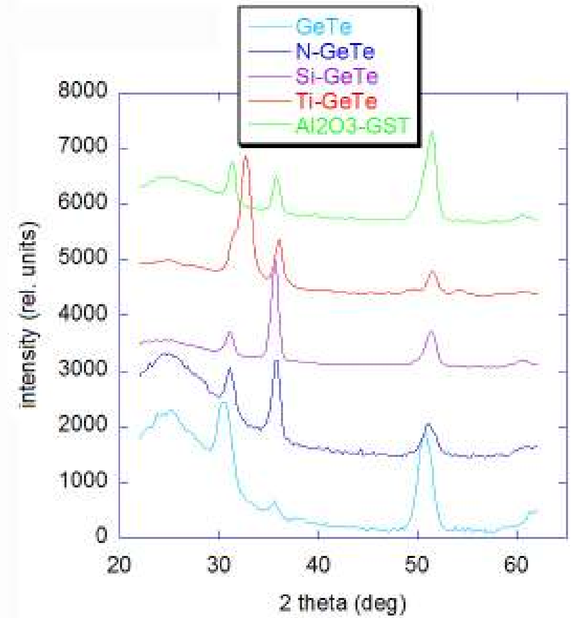


Figure 3: θ-2θ scans of undoped and doped GeTe after a ramp to 450 ºC.

Figures 4 and 5 show the resistivity as a function of temperature for undoped and doped GST and GeTe, respectively.

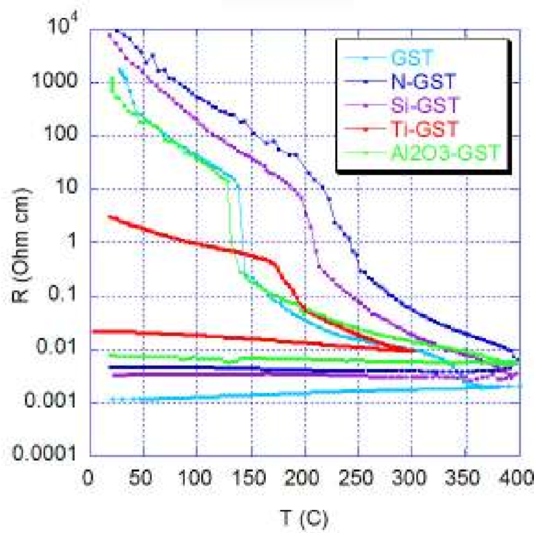


Figure 4: Resistivity as a function of temperature for undoped and doped GST.

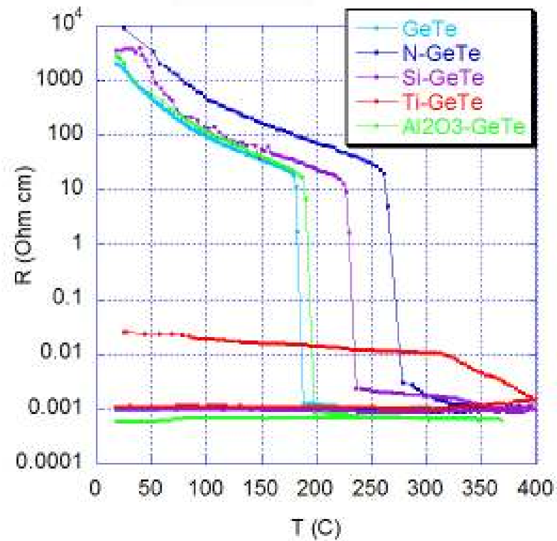


Figure 5: Resistivity as a function of temperature for undoped and doped GeTe.

Crystallization temperatures determined by resistivity vs. temperature measurements, indicated by a more or less sharp drop in resistance, agreed within a few degrees with crystallization temperatures measured by time-resolved XRD measurements, indicated by the appearance of XRD peaks. For GST the values of the resistances in the amorphous phase and the crystalline phase were increased for all dopants except for Ti doping that led to a substantial decrease in the resistance of the amorphous phase and therefore the electrical contrast. The more gradual transition for N-GST seen in the XRD data is also reflected in the resistivity vs. temperature measurements. For GeTe, nitrogen doping increased the resistance in the amorphous phase and Ti doping reduced the resistivity in the amorphous phase even more drastically than in the case of GST. The other resistance values for doped GeTe were not much influenced.

Figure 6 shows a schematic and a micrograph of the PCRAM cells (before deposition of the top contact).

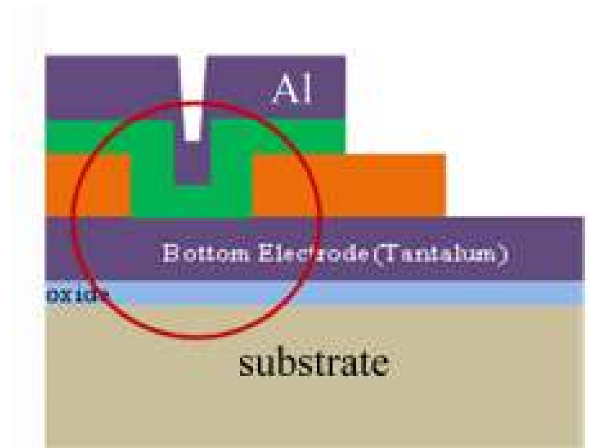


Figure 6: Schematic of PCRAM cell.

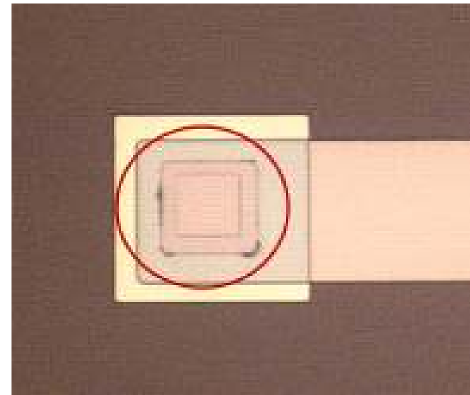


Figure 7: Micrograph of PCRAM cell.

Figure 8 are transmission electron microscopy (TEM) images of the fabricated PCRAM cell. Figure 9 is an EDAX scan across the phase change material, undoped GST in this case, in the direction indicated by the red line in the right panel of Figure 8. It shows good uniformity of the GST composition and a ratio of Ge:Sb:Te close to 2:2:5. A thick layer of Cr was sputtered before the TEM sample preparation using focused ion beam. Because the TEM sample was mounted on a Cu grid, there is a constant Cu x-ray signal in the background. Due to the peak overlapping between Cu and Ta, the Ta signal in the Cr and GST layer could be an artifact.

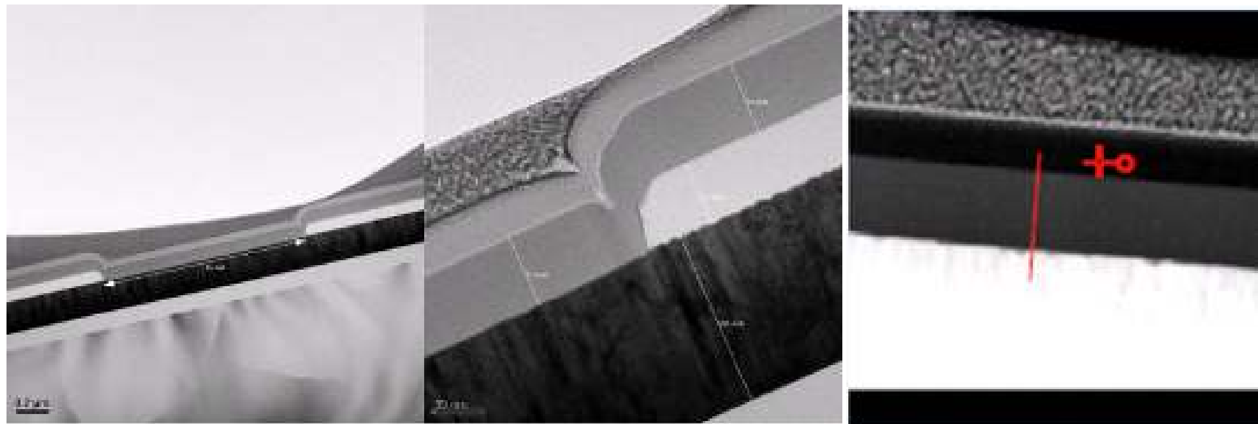


Figure 8: Transmission electron microscopy images of the fabricated PCRAM cell. The red line in the right panel indicates the direction of the EDAX scan (Figure 9).

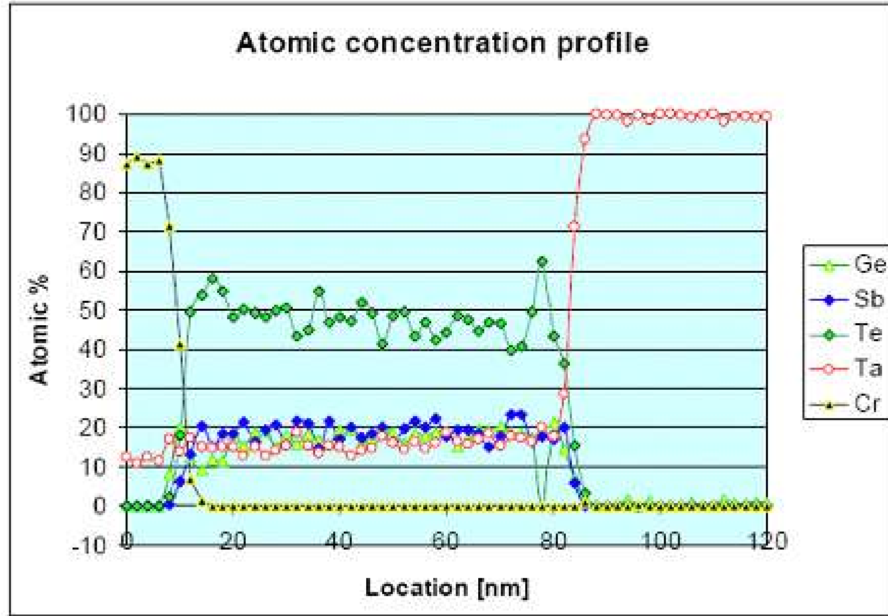


Figure 9: EDAX scan (direction indicated by red line in Figure 8).

Electrical testing of these devices showed threshold switching for all materials. The threshold voltage and thus the threshold field were found to be a function of phase change material and dopant. Undoped GST showed a threshold field of 60 V/µm, in good agreement with values reported in the literature [10]. Undoped GeTe had a substantially higher threshold field of 143 V/µm. High threshold fields are desirable for ultra-scaled devices because for a very small size of the amorphous region, the threshold voltage might become comparable to the reading voltage and the reading operation would disturb the state of the cell. For GST, doping with nitrogen and titanium had little effect, silicon led to a small increase and the largest increase was observed for aluminum oxide doping (60% increase). For GeTe, titanium and aluminum oxide doping reduced the threshold field while silicon and nitrogen doping increased it. Nitrogen-doped GeTe had the highest threshold field of around 248 V/µm, a 73% increase compared to undoped GeTe. This is the highest threshold field of any material we are aware of. Table II summarizes the data for the threshold field of the various phase change materials.

Phase change material	Dopant	Threshold Field (V/µm)
GST	None	60
GST	N	70
GST	Si	79
GST	Ti	58
GST	Al_2O_3	96
GeTe	None	143
GeTe	N	248
GeTe	Si	193
GeTe	Ti	60
GeTe	Al_2O_3	70

Table II: Threshold field in PCM cells fabricated using films of this study

4. CONCLUSIONS

We have characterized crystal structure, crystallization temperature, resistances in the amorphous and crystalline phase and threshold field for a variety of dopants in the phase change materials GeTe and GST. For GST, of all the dopants measured, nitrogen was the most successful in terms of modifying materials parameters that are beneficial for PCRAM applications leading to an increase in crystallization temperature (good for data retention) and increase in resistances (reduction in RESET current). Aluminum oxide doping had the largest effect for increasing the threshold voltage (important for device scaling). For GeTe phase change material, titanium doping led to the highest crystallization temperature, but it also strongly reduced the electrical contrast. Nitrogen appears to be a better candidate: it also increases the crystallization temperature substantially and leads to higher threshold fields. Dopants still need to be identified that raise the resistivities of GeTe, in particular in the crystalline phase. Further studies are required to investigate the influence of the dopants on the crystallization times and to study their behavior with respect to elemental segregation which is an issue for PCRAM cell cyclability [11]. Doping can however in fact reduce segregation and void formation and thus improve device performance [12].

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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.

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Christopher M. Breslin received his B.S. degree (2005) in Computer Science and Applied Mathematics and his M.S. degree (2011) in Nanoscale Science & Engineering from SUNY Albany. His master's thesis project consisted of developing a model to determine the effects of secondary electron emission characteristics on charged matter beam induced depositions. He currently holds a position at the IBM T.J. Watson Research Center supporting advanced research projects through TEM preparation and TEM preparation development techniques.

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.