

# Direct Observation of Structural Changes Leading to RESET state drift in Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>

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## ABSTRACT

Phase-change memory stores data in the form of structure rather than charge. This form of storage has many advantages relating to scaling as processing technology advances to smaller dimensions and the scaling limits of charge based storage are reached. The large change in resistance values between the SET and RESET state also holds the possibility of enabling multi-level storage in a single location, however, resistance drift towards larger resistance values after the formation of the high-resistance RESET phase complicates the use of multilevel storage. It has been speculated that stress relief and unidentified structural relaxation mechanisms may be behind the resistance drift, but to date, no direct observations of the structural changes that occur during the drift process have been reported. We have used x-ray absorption spectroscopy (XAFS) at both the Ge K and L3 edges to observe changes in local structure as a function of thermal treatment of sputter deposited Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> layers and have correlated these measurements with resistance drift. We show that the structural relaxation is due to a gradual transformation of higher energy tetrahedral bonds into octahedral bonds with upon the structural relaxation of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>.

**Key words:** resistance drift, x-ray absorption, structural changes

As the need for denser and less power hungry nonvolatile memory continues to increase, industry has met the challenge by shrinking die sizes with each successive fabrication node. The current generation of nonvolatile memory, as epitomized by FLASH memory, is based upon the storage of charge and is facing significant challenges as the amount of charge stored per bit continues to decrease with each development node, making further improvements in memory cost based upon advances in scaling alone more challenging. Phase-change memory on the other hand as exemplified by the alloy Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> (GST), stores information via structure and studies suggest even for films as thin as a nanometer, both the SET and RESET phases are stable and the crystallization temperature remains unchanged from that of thicker films providing appropriate encapsulation is used [1]. The large, more than two orders of magnitude increase in resistivity between the SET and RESET states in GST also holds the promise of enabling multilevel storage in a single location. An issue complicating the use of this large change in resistivity for multilevel storage is the observation that after the transition to the RESET state, the resistance of GST continues to *increase* for following a power law for a given temperature for up to an order of magnitude. The origin of resistance drift has been the subject of much speculation and some of the proposed underlying mechanisms include structural relaxation and release of strain. It has also been reported that the optical bandgap increases in concert with the change in resistance. In the current work, we have characterized the resistance drift in a variety of GST samples and using the same process parameters, have measured the changes in local order using x-ray absorption spectroscopy (XAFS) at the Ge L3 and K absorption edges. XAFS is well suited to observe changes occurring during drift as the coherence length of the probe is on the order of 1-2 nm, distances over which structural changes induced by thermal activated processes occur.

For the experiment a series of 300 nm thick GST samples were deposited by RF magnetron sputtering onto Si substrates upon which an electrically insulating SiO<sub>2</sub> thermal oxide had been grown. The original wafers were cut into individual pieces about two centimeters on a side. Upon one set of samples, electrical contacts were deposited and the electrical resistance was characterized as a function of annealing time. The measured change in electrical

resistance was found to fit a power law as has been described in the literature. Typical resistance change for a one day anneal at different temperatures is shown in Figure 1. A clear trend in resistance drift with annealing temperature can be seen.

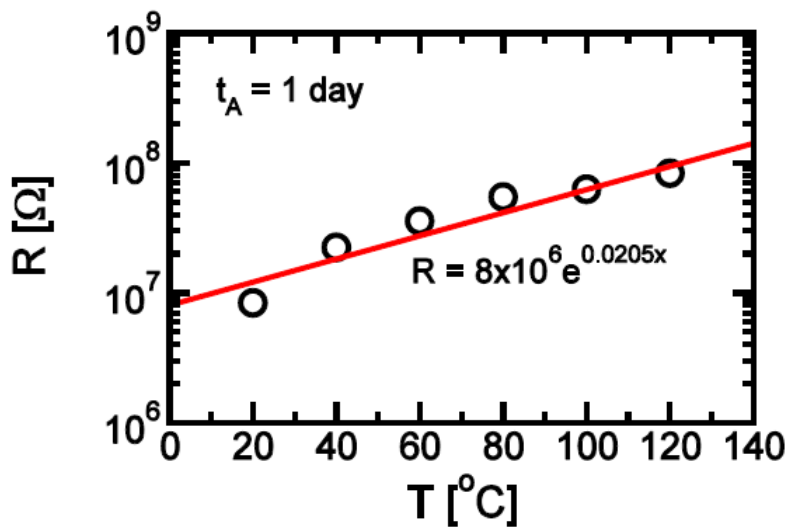


Figure 1. Measured change in resistance for amorphous GST as a function of annealing time.

XAFS studies were carried out on the same set of samples. Figure 2 shows Ge L3 absorption edge structure for the same amorphous samples as a function of annealing temperature for a three hour annealing treatment. A clear shift in the absorption edge structure with annealing temperature can be seen. The change in the edge structure observed has been studied earlier using ab-initio relaxed structures and their corresponding XAFS spectra using the all-electron code Wien2K [2]. This work concluded that the change in the edge feature observed in the resistance drift samples originates from a transformation of local bonding units from tetrahedral to octahedral geometries. We have also studied the same set of samples using the Ge K-edge and observed changes in the XAFS signal indicative of the trend from tetrahedral to octahedral structural units.

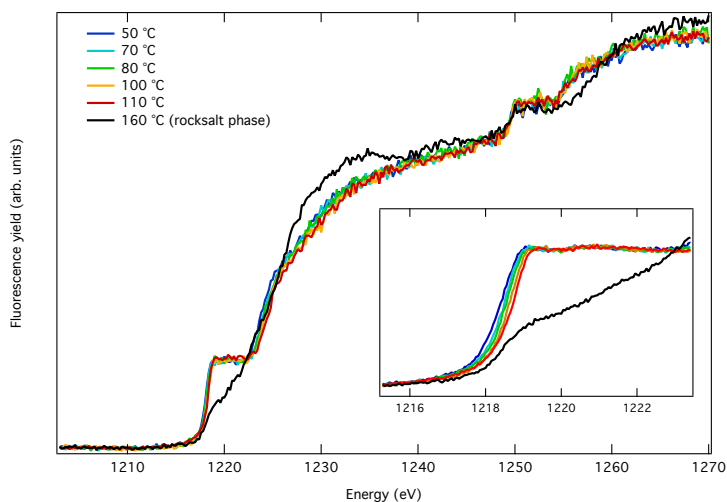


Figure 2. Ge L3 Edge spectra of amorphous GST layers thermally treated for three hours at various temperatures.

We conclude that the resistance drift occurring in GST is a result of changes in local order as manifested by a change in local bonding geometry from tetrahedral to octahedral geometries. Stress is thus concluded not to play a major role in the resistance drift mechanism. Further details of the relaxation process will be reported.

## REFERENCES

- [1] R. E. Simpson Nano. Lett., **10** (2010) 414
- [2] M. Krbal et al., Appl. Phys. Lett., **102** (2013) 111904

## Biography

Paul Fons graduated from the University of Illinois at Urbana-Champaign in 1990 writing his thesis on the growth and electronic structure of metastable semiconductor alloys. Subsequently, he became a research fellow at the University of Tsukuba in Japan. In 1993, he joined the National Institute of Advanced Industrial Science & Technology (AIST) also located in Tsukuba. While at AIST, he has carried out extensive work in molecular beam epitaxy, photoluminescence, and structural measurements using synchrotron radiation including diffraction, x-ray absorption, and high-pressure, and ultra-fast time-resolved synchrotron studies as well as density-functional theory calculations. He is currently working in the functional materials group at AIST on phase-change materials.