Chalcogenide semiconductor phase-change materials (PCMs) were first introduced in 1968 by Stanford Ovshinsky and later commercialized in the early 1990’s for rewritable optical data storage devices. Data are encoded on PCMs as a series of crystalline and amorphous marks corresponding to binary 0’s and 1’s, respectively. Unlike other semiconductors, the crystalline and amorphous states of PCMs have drastically different optical and electrical properties: the crystalline phase has low resistivity and high reflectivity, whereas the amorphous phase has high resistivity and low reflectivity. These differences allow the data to be read easily. The crystalline-to-amorphous phase transition can be induced by applying a current pulse to the material. The write/read/erase cycle is illustrated in Figure 1. Data are written by applying a short pulse (100 ns) of large current to the crystalline material. Resistive heating resulting from the pulse raises the temperature above the melting point, and subsequent rapid quenching forms an amorphous region. Data are erased by recrystallizing the amorphous region using a longer pulse (300 ns) of a lower current to heat the material above the glass transition temperature but below the melting point.

One PCM currently used in rewritable media is Ge$_2$Sb$_2$Te$_5$ (GST). GST exhibits two crystalline states: a metastable distorted rocksalt phase and a stable hexagonal phase. For the purpose of PCMs, the phase change of interest is the amorphous-to-rocksalt transition, which occurs around 130 °C. In the distorted rocksalt structure, Te atoms occupy one FCC lattice and Ge/Sb atoms occupy another sublattice. The Ge/Sb sublattice intrinsically has ~20% vacancies which remove antibonding states and decrease the energy of the structure. EXAFS experiments and simulations indicate that the Ge atoms are octahedrally coordinated in the crystalline state with three longer Ge-Te bonds and three shorter Ge-Te bonds. During the phase transition, the three longer Ge-Te bonds are broken and the Ge atom undergoes an “umbrella flip” to become tetrahedrally

**Figure 1:** Resistance change as a function of writing current.
coordinated in the amorphous phase (Figure 2). The shorter, stronger Ge-Te bonds give the amorphous phase more local order than the crystalline phase and thus relatively stable, making GST a suitable material for data storage.

![Crystalline to Amorphous Phase Transition](image)

Figure 2: Ge coordination in crystalline-to-amorphous phase transition.

One shortcoming of PCM thin films is the presence of lithographic defects that cause rapid recrystallization and data loss. Such defects can be avoided by using PCM nanowires because of their sub-lithographic size and single-crystalline nature. Nanowires are known to have lower melting points than their corresponding bulk material. The melting point of nanowires can be determined by resistively heating a sample in a high resolution TEM and measuring the temperature at which the electron diffraction pattern disappears. Sun et al. observed a 46% decrease in melting point for 40-80 nm GeTe nanowires. This is an advantageous property for PCM devices because a smaller current (i.e. less resistive heating) is required for the phase transition, thus decreasing the power consumption. The dependence of the writing current on nanowire size was studied by Lee et al. Thinner nanowires require smaller writing currents: a 200 nm GST nanowire requires a 1.3 mA writing current, whereas a 30 nm nanowire requires only 0.16 mA. Additionally, a 100 nm “top-down” GST cell requires a 1.5 mA writing current, whereas a 100 nm GST nanowire requires 0.4 mA.

Two important concerns regarding the use of nanowires as PCM devices are cyclic durability and data retention. Write/read/erase cycles were applied continuously to a GST nanowire device to test its durability. Cycling-induced failure was not observed until >10⁵ cycles; this durability is comparable to current rewritable media. Data retention abilities were tested by keeping different diameter amorphous nanowires under isothermal conditions and waiting for them to recrystallize (signifying data loss). Smaller nanowires recrystallize faster. This observation is consistent with conventional thermodynamics which predicts a lower activation energy barrier for heterogeneous nucleation from surfaces; this effect is more pronounced in smaller diameter nanowires. A 60 nm nanowire is expected to be able to retain its amorphous nature for ~ 25 years at 80 °C.

References


