

## 10-1 Untangling the Mystery of Re-writable Optical Recording

Re-writable optical recording got its start in the 1960's with the suggestion of Ovshinsky of using the crystalline/amorphous phase transition in multi-element chalcogenide compounds for memory [1]. Although IBM carried out promising early efforts in the 1970's, it was the work of Matsushita which culminated in the development of optical disks capable of more than a million re-write cycles [2]. Based upon these early developments, the 4.7 GB digital versatile disk random access memory (DVD-RAM) was successfully commercialized and is now the foundation of a major industry. A comprehensive search for the best phase change memory alloys in terms of performance and reliability resulted in the selection of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  (DVD-RAM) and  $\text{Ag-In-Sb-Te}$  (DVD-RW) alloys. In this report, we focus on  $\text{Ge}_2\text{Sb}_2\text{Te}_5$ .

Recording in optical disks utilizes (higher-reflectivity) amorphous marks on a (lower reflectivity) polycrystalline background. Amorphous, crystalline, regions as well as readout are accomplished with a single laser with crystallized regions created by laser heating to a temperature just above the glass-transition temperature, while amorphous regions are generated using higher power, short laser pulses rapidly quench the  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  from temperatures above the melting point forming amorphous material. Minimum quench rate estimate range as high as  $10^{12}$  K/s with switching times into the amorphous states on the order of nanoseconds [3]. It is ironic that, a multibillion dollar industry has been built up around this technology, but until recently little was known about the details of the structural transition behind the process.

Starting with a structure determined by powder diffraction for the crystalline phase, we have used X-ray absorption spectroscopy (XAFS) to investigate the key local changes in local structure responsible for the unique properties. We used BL-12C for the Ge edge and SPring-8 for the Sb and Te edges. Rietveld fitting results indicated  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  crystallized in the rocksalt ( $\text{Fm}\bar{3}\text{m}$ ) structure with Ge/Sb on 4a and Te on the 4b site with (0.4/0.4) and 1.0 occupancy, respectively. Careful XAFS measurements at the K-edges of all three elements of the crystalline phase demonstrated the presence of three short and three long Ge-Te and Sb-Te bonds reminiscent of the bonding in the binary GeTe with the second nearest-neighbor Te-Te distances the same as that determined by XRD. From these XAFS results, the structure of the fundamental building block was developed as shown in Fig. 1. Similar measurements clearly revealed an unusual *increase* in short-range order in moving from the crystalline to the amorphous phase. Ge-Te and Sb-

Te bond lengths changed from 0.283 and 0.291 nm to 0.261 and 0.285 nm, respectively. The key mechanism behind the transformation is illustrated in Fig. 2 in which Ge atoms undergo a change in coordination from a distorted-rocksalt like structure to their preferred tetrahedral coordination. The stochastic nature of the switch and the strengthening of *short-range* order induces relaxation of the Te unit cell destroying the long-range order that is effectively probed by diffraction techniques. We refer to this transformation as “an umbrella” flip of Ge and is a result of the preferential breaking of the longer Sb-Te and Ge-Te bonds. It is this diffusion-less transformation and the preservation of the Te sublattice (with some relaxation) that ensure that the transformation process is fast and reversible. Further details can be found in our paper [4].

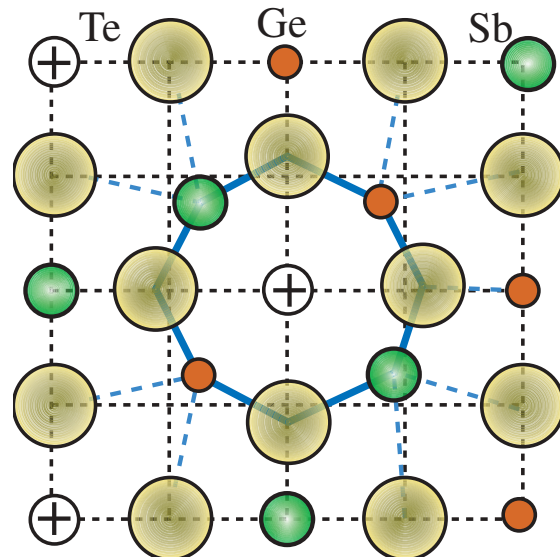


Figure 1

A simplified building block from which the structure of the crystalline phase can be constructed. The white circles represent vacancies which assume a net positive charge and via coulombic repulsion give rise to the structure shown.

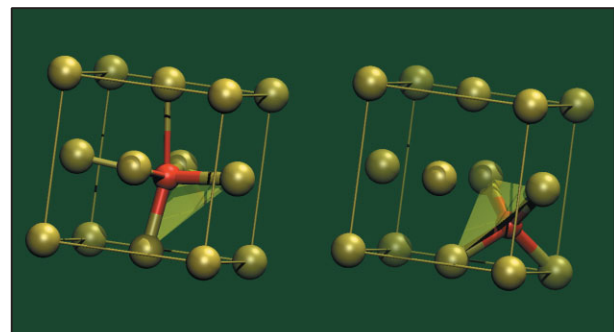


Figure 2

A simplified view of the crystalline and amorphous structure showing only Te (tan) and Ge (red) atoms demonstrating the “umbrella flip” of Ge coordination underlying the phase transformation from the crystalline to amorphous phase.

**References**

[1] S. R. Ovshinsky, *Phys. Rev. Lett.*, **21** (1968) 1450.

[2] T. Ohta, *J. Optoelectron. Adv. Mater.*, **3** (2001) 609.

[3] V. Weidenhof, N. Pirch, I. Friedrich, S. Siegler and M. Wuttig, *J. Appl. Phys.*, **88** (2000) 657.

[4] A. V. Kolobov, P. Fons, J. Tominaga, A. Frenkel, A. L. Ankudinov and T. Uruga *Nature Materials*, **3** (2004) 703.