

## Photoassisted amorphization of the phase-change memory alloy $\text{Ge}_2\text{Sb}_2\text{Te}_5$

P. Fons,<sup>1,2,\*</sup> H. Osawa,<sup>2</sup> A. V. Kolobov,<sup>1,2</sup> T. Fukaya,<sup>1</sup> M. Suzuki,<sup>2</sup> T. Uruga,<sup>2</sup> N. Kawamura,<sup>2</sup> H. Tanida,<sup>2</sup> and J. Tominaga<sup>1</sup>

<sup>1</sup>*Nanodevice Innovation Research Center (NIRC), National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8562, Japan*

<sup>2</sup>*Japan Synchrotron Radiation Research Institute, Kouto, Sayo, Hyogo 679-5198, Japan*

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Subnanosecond time-resolved x-ray absorption measurements have been used to probe dynamical changes in the local structure about Ge atoms in the phase-change alloy  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  during the optical recording (amorphization) process using an optical pump and x-ray probe technique to examine the reversible phase transition from the metastable crystalline phase to the amorphous phase. We provide unambiguous evidence that the amorphization process *does not* proceed via the molten state but is a photoassisted process. We argue that the transition to the amorphous phase is a consequence of photoassisted destabilization of the resonant bonding present in the crystalline phase. This observation challenges the currently existing paradigm of the phase-change process which implicitly assumes the existence of the molten phase as a prerequisite for the creation of the amorphous phase. Implications from this finding are discussed, including the possibility to use the polarization of light as an extra coordinate for data recording.

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Ultrafast photoinduced processes have long been a focus of research with the goal of creating fast and stable, nonvolatile optical memories. In recent years, this effort has broadened to include nonvolatile electrical memory. In commercial optical storage applications, years of research has led to the selection of Te-based phase-change memory (PCM) alloys such as Ge-Sb-Te and Ag-In-Sb-Te; the composition  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  (GST) is used for DVD-RAM applications.<sup>1</sup> In optical memory, information is stored as amorphous marks on a crystalline background while in electrical memory, information is stored in the form of resistivity. The amorphous phase representing the *reset* state has high resistivity while the lower resistivity crystalline phase represents the *set* state. The amorphous phase in both cases is generated by the application of a short, intense pulse of light or current for optical or electrical memory, respectively. Recently, interest in these materials has further intensified due to the fact that the currently widely used FLASH memory is approaching a bit size limit when a single electron will be used to store information.<sup>2</sup> At the same time, Te-alloy-based phase-change memories possess significantly better scaling characteristics that allow for further increases in memory density. As GST is both currently one of the leading commercial rewritable optical memory materials and is also the leading contender for electrical memory applications, in this Rapid Communication we choose to focus on GST as a prototypical phase-change alloy. One of the major requirements for developing new memories is high switching speed.

Reflectivity changes associated with the laser-induced amorphization of GST occur on the order of nanosecond,<sup>3</sup> but the speed at which the *structural transition* actually takes place has remained unclear. On the one hand, femtosecond pulses have been shown to amorphize GST which suggests that the amorphization process may be as short as femtosecond time scales.<sup>4</sup> On the other hand, time-resolved optical studies have shown that changes in reflectivity involve two decay components, a faster component of about 1 ns, and a slower component of about 10 ns.<sup>3</sup> Clearly, none of the aforementioned experiments have provided direct evidence

for the structural change duration which could be somewhere in between tens of femtosecond and tens of nanosecond—a rather large range which has to be narrowed down.

The stable phase of crystalline GST is a nine-layer rhombohedral structure with no intrinsic vacancies. PCM applications of GST, however, utilize a *metastable* crystalline phase as one side of the phase-change cycle. The average structure of this phase is rocksalt, with the Te atom fully occupying one fcc sublattice with 40% Ge, 40% Sb, and 20% vacancies on the other fcc sublattice. X-ray absorption measurements of the crystalline structure have revealed the presence of a rhombohedral distortion in the cubic crystalline phase which breaks the symmetry of the six identical bonds of octahedral coordination into three short and three long bonds<sup>5</sup> leading to a bonding hierarchy with sets of longer (weaker) and shorter (stronger) bonds existing between the center atom and its two colinear nearest neighbors. The observation that the  $3s^23p^2$  electron configuration of Ge in the presence of the *p*-type bonding of the rocksalt structure cannot have all saturated bonds has led to the concept of *resonant bonding* in IV-VI compounds in which covalent bonds are saturated by virtue of electrons shared with nearby atoms;<sup>6</sup> this concept was further elaborated upon in Ref. 7. In contrast, the amorphous phase is characterized by shorter covalent bonds where the local coordination is well described by Mott's 8-N rule; strong local distortions in the amorphous phase destroy long-range order. PCM applications take advantage of the large optical and electronic differences spawning from the above large changes in bonding between the phases.

The presence of a bond hierarchy in the resonantly bonded crystalline phase causes the crystalline phase to be unstable with respect to externally induced disorder which in turn leads to the formation of the amorphous phase which is characterized by conventional covalent bonding.<sup>7</sup> In addition, the random distribution of vacancies in the metastable crystalline phase breaks translational symmetry and leads to behavior reminiscent of molecular crystals in which bonding and antibonding states are partially localized. This leads to the unusual situation where the presence of a nonequilibrium

electron distribution can lead to the selective destruction of the longer bonds and in turn the destabilization of the *meta-stable* crystalline phase. Such electron distributions can exist in high concentrations during the recording process either as a result of electron-hole pair generation or carrier injection from a contact. They necessarily modify the interatomic potentials and may affect the phase-change process as suggested, for example, in Ref. 8. While athermal melting has been reported for various materials when intense ultrashort (femtosecond) excitation pulses were used,<sup>9,10</sup> for device-relevant pulse durations in the nanosecond range, it has generally been implicitly assumed that the role of the pulse is simply to generate heat and melt the material that is subsequently quenched into the amorphous phase. We emphasize here that the process we are describing is distinct from athermal melting in stable structures in which extremely large distortions in the electron energy distribution generated by sources such as femtosecond lasers give rise to lattice instabilities. In contrast, the crystalline state of GST is intrinsically metastable and the presence of significant disorder allows significantly smaller deviations from equilibrium carrier distributions to lead to photoassisted destabilization of the crystalline phase.

Time-resolved structural studies of the amorphization process in phase-change materials are essentially nonexistent. One possibility to look at the amorphization process would be to use time-resolved x-ray diffraction but this approach has fundamental limitations. Since sharp diffraction peaks in the crystalline state are a direct consequence of long-range order, any observation of the disappearance of diffraction peaks would be a measure of the loss of long-range order but would not necessarily mean that the structural relaxation is complete; the structure may well continue to evolve further after the long-range order has been lost. In addition, as Bragg diffraction only detects average order, the presence of site disorder limits the ability of such diffraction-based techniques to distinguish between average structure and actual individual bonds lengths.<sup>11</sup>

A unique technique to *directly* investigate the kinetics of structural relaxation is x-ray absorption spectroscopy. By measuring the x-ray absorption fine structure (XAFS) spectra with the needed time resolution, one can get information about changes in the electronic and atomic structure. In addition, XAFS can be applied on an equal basis to both the crystalline and amorphous phases. The femtosecond order time-resolution lifetime of the core hole limits the time resolution of XAFS to the duration of the x-ray excitation source ( $\sim 50$  ps in the current study).

An optical pump and x-ray probe technique that is capable of the acquisition of XAFS spectra with sufficient time resolution makes possible the direct observation of the structural evolution on subnanosecond time scales. A general description of the setup has been given elsewhere.<sup>12</sup>

In the present Rapid Communication, we report on subnanosecond time-resolved x-ray absorption near-edge structure (XANES) observations of the recording (amorphization) process. Unlike extended x-ray absorption fine structure where oscillations quickly damp with temperature, XANES is insensitive to temperature (see Fig. 1, left) and at the same time is highly sensitive to the three-dimensional structure

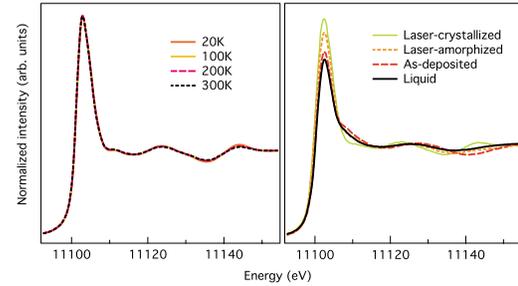


FIG. 1. (Color online) Independence of XANES spectra (e.g., crystalline  $\text{Ge}_2\text{Sb}_2\text{Te}_5$ ) on temperature (left) and pronounced differences among XANES spectra for laser-crystallized (green thin solid line), laser-amorphized (orange fine dashed line), as-deposited (red course dashed line), and liquid (black thick solid line)  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  (right) make XANES a robust probe of the structure present.

present. The strong multiple-scattering regime of XANES provides a unique and robust signature of the three-dimensional structure present about the absorbing atom within a radius of a few nanometer.<sup>13</sup> In this experiment, we made use of the fact that the white-line intensity (WLI) of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  is significantly different among the crystalline, amorphous, and liquid states<sup>14,15</sup> as shown in Fig. 1, right and can serve as a signature of the structure present. [The term “white line” refers to the peak immediately after the absorption edge (about  $\sim 11\,103$  eV in this case).]

As an example of the utility of using the WHI to probe the local structure, a three-dimensional area map of the fluorescence intensity at the x-ray excitation energy corresponding to the white-line position of Ge is shown in Fig. 2. The recorded (amorphized) and erased (crystallized) areas can be clearly distinguished using XAFS spectroscopy. It should be mentioned here that the 600 ps duration of the recording pulse was chosen so as to be short enough to allow time-

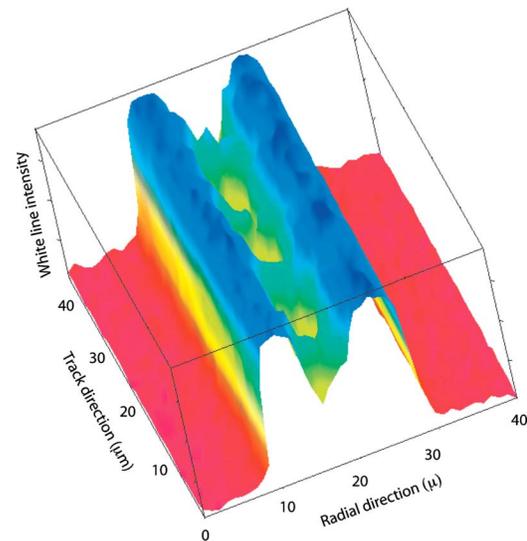


FIG. 2. (Color online) A three-dimensional x-ray intensity map showing the crystallized band [blue (dark gray)], small amorphous marks [yellow (light gray)], and as-deposited amorphous background [red (intermediate gray)]. An approximately  $1\ \mu\text{m}$  diameter x-ray probe was used.

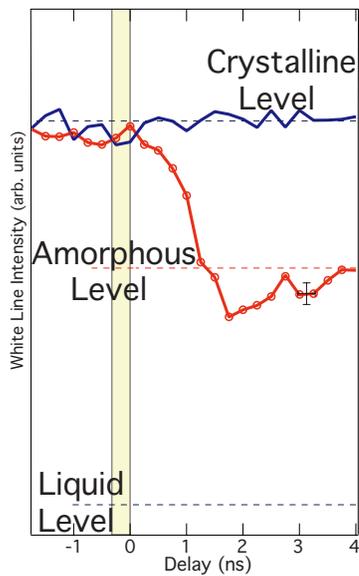


FIG. 3. (Color online) Time evolution of the fluorescence intensity at the white line. A decrease in the WLI following the excitation process is followed by a slower partial recovery. While the steady-state WLI reaches exactly the static amorphous value, the minimum intensity is *significantly higher* than the corresponding WLI value for the liquid phase demonstrating that  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  *does not melt* in a conventional sense on its way to the amorphous phase. The yellow rectangle indicates the duration and relative position of the excitation pulse and the cross bar indicates the estimated error on both axes. Data points have been indicated on the amorphizing intensity trace.

resolved measurements to be carried out but long enough to allow thermalization of photoexcited carriers ensuring that the underlying physics of the switching process is similar to that used in optical and/or electrical devices and which, as mentioned above, is commonly believed to be thermal in nature.

Figure 3 shows time evolution of the WLI of GST as a function of delay after the excitation pulse. To exclude the possibility of a baseline shift, we simultaneously monitored the corresponding intensity one-electron orbit period before ( $\sim 5 \mu\text{s}$ ) the laser pulse, i.e., in the starting crystalline state; no change in baseline was observed. One can clearly see from the figure that following exposure to the laser pulse, the WLI first monotonically decreases and reaches a minimum value in about 1 ns. This fast initial decrease in WLI is followed by its partial recovery and within  $\sim 2$  ns a new saturation value is reached. Scans, corresponding to longer time delays (not shown), confirm that the white-line intensity remains unchanged for delay times greater than 4 ns after the amorphizing pulse. This final value coincides with the value of the WLI in the amorphous state realized after exposure to a laser pulse.

It is of particular interest that the minimum value of the WLI during the amorphization process is *significantly higher* than that corresponding to the static liquid state<sup>15</sup> clearly demonstrating that  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  does not melt in a conventional sense upon its transformation from the crystalline to the amorphous phase. This finding demonstrates that the

amorphization process in the subnanosecond excitation regime is different than what has been believed so far and *does not* consist of thermal melting and subsequent quenching of the melt into the amorphous phase.

While athermal melting of solids has been previously observed in various semiconductors, we would like to note two aspects that make our result fundamentally different. First, in previous studies, much shorter (femtosecond) pulses were used and the nonthermal melting observed was explained by a high population of excited carriers in the conduction band that softened the interatomic potential allowing for significant atomic diffusion at low temperatures.<sup>9,10</sup> Second, the nonthermal melting by femtosecond pulses was observed in covalently bonded semiconductors where all bonds are identical.

Phase-change materials, on the other hand, are special in a sense that while they are semiconductors, there are two kinds of bonds between identical pairs of atoms, namely, in the locally rhombohedrally distorted structure there are subsets of shorter (stronger) and longer (weaker) Ge(Sb)-Te bonds. These structures are usually described as Peierls distorted with resonant bonds. The other distinctive difference is that we have used pulses with duration longer than the carrier thermalization time.

We believe that the peculiar behavior of GST arises from the presence of resonant bonds. When we excite such a solid, the occupation of low-lying states in the conduction band further weakens already weakly bonded atoms and—in the presence of thermal vibrations of sufficient amplitude—the weak resonant bonds that exist in the crystalline phase are likely to break leading to a reorganization of the solid network. Such a description of charge localization is reasonable due to the large amount of local site disorder present in GST. We argue that it is the presence of this bond-energy hierarchy that makes it possible to selectively excite the weaker bonds and reach photomelting conditions using more than a factor of five less fluence than that in semiconductor laser-recording studies.<sup>16</sup> Even though we populate a significantly lower total number of states in the conduction band, we selectively—and almost exclusively—populate the low-energy states associated with the weaker bonds. These states are populated after electrons thermalize to the bottom of the conduction band, i.e., when thermal equilibrium in the system has been reached, which explains the observed times significantly exceeding the femtosecond time scale.

We would like to note a similarity between the athermal nature of the amorphization process of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  unveiled by our time-resolved XAFS studies and laser-induced melting of selenium reported earlier.<sup>17</sup> By the use of Stokes and anti-Stokes Raman scattering, it was unambiguously demonstrated that the melting process was athermal. Selenium is a molecular crystal consisting of spatially ordered helical chains held together by a weak van der Waals interaction which is analogous to the short (strong) and weaker (long) bonds of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$ . As has been demonstrated, photoexcitation leads to rupture of interchain Se-Se bonds and subsequent loss of the chain ordering.

A related effect, a significant athermal photoinduced decrease in viscosity associated with increased atomic motion has been reported in amorphous  $\text{As}_2\text{S}_3$  (Refs. 18 and 19)

whose structure also contains stronger and weaker bonds. Molecular-dynamics simulations<sup>20</sup> have revealed that atomic diffusion in amorphous  $\text{As}_2\text{S}_3$  can be enhanced over 1 ps by promoting one (of 1204) active electron above the lowest unoccupied molecular orbital level and it was suggested that this process can potentially lead to photomelting.<sup>20</sup> We would also like to note that photomelting of the self-organized state of the backbone to a random network has also been reported for compositions in the Ge-Se system that are close to the rigidity transition.<sup>21</sup>

We believe that the amorphization of GST and the photo-induced phenomena in  $\text{As}_2\text{S}_3$  and Se have a common nature, namely, in both cases photoexcitation results in preferential rupture of the weaker (sacrificial) bonds due to large electron population occupying low-energy states in the conduction band thus allowing for significant structural relaxation that ultimately leads to the loss of long-range order. We speculate that this phenomenon can be generalized to other solids with a similar asymmetry in bond strength.

While in this study, we have demonstrated that the crystalline-to-amorphous transition does not involve conventional melting in the case of laser excitation, we believe that the process is very similar for electrical memories when a large concentration of nonequilibrium carriers is injected into  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  from a contact. These charge carriers predominantly populate states arising from antibonding states of the weaker resonant bonds eventually resulting in their rupture and leading to the collapse of resonant bonding. It thus appears that the presence of sacrificial bonds whose rupture leads to collapse of the ordered phase is crucial for fast switching in phase-change materials and this factor must be taken into account in the search for new materials. While no data for the radiative lifetimes of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  or GeTe can be found in the literature, we note that the experimental radiative lifetimes in the IV-VI semiconductors PbTe and PbSbTe

are on the order of nanosecond<sup>22</sup> suggesting that the 600 ps duration of the excitation pulse may lead to a significant population inversion consistent with the above sacrificial bond concept.

The fact that the transformation process does not consist of melting but takes a route via a photoexcited state opens different possibilities for data storage. In particular, the use of linearly polarized light of the appropriate wavelength may result in the spatially selective rupture of bonds thus opening the possibility of further increasing recording density.

In summary, we have performed local structure measurements on a subnanosecond time scale of the phase-change recording process. Our measurements unambiguously demonstrate that contrary to the current consensus, the crystal-to-amorphous transition *may not* involve conventional melting but proceeds through a photoexcited state that, we argue, triggers rupture of sacrificial (resonant) bonds leading to collapse of the ordered phase. We argue that these findings offer an alternative interpretation of the phase-change process in this class of materials and also suggest that functional phase-change materials should possess a bond-energy hierarchy. While the results of the current experiment are only directly applicable to Ge-Sb-Te-based alloys, we speculate that the presence of a bond hierarchy that is a general trend in many Te-based PCM alloys may broaden the applicability of the current results to other alloys. The current results also suggest a way of further increasing memory density through the use of linearly polarized light.

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\*paul-fons@aist.go.jp

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