

Structure of the amorphous phase and the amorphisation mechanism in Ge-Sb-Te alloys

A.V. Kolobov^{1,2}, P. Fons^{1,2}, M. Krbal¹, and J. Tominaga¹

¹National Institute of Advanced Industrial Science & Technology, Tsukuba Central 4, Higashi 1-1-1, Tsukuba, Ibaraki, 305-8562, Japan

²SPring8, Japan Synchrotron Radiation Institute (JASRI), Kouto 1-1-1, Sayo-cho, Sayo-gun, Hyogo 679-5148, Japan

ABSTRACT

Insightful development of new materials for phase-change memories require understanding of the phase-change mechanism and the origin of the contrast properties between the crystalline and amorphous phases. This understanding, in turn, is impossible without precise knowledge of the structure and bonding nature in the two phases. In this work, recent results obtained by the authors are reported.

Keywords: excited-state pathways, density-functional theory, GeTe, amorphisation

1. INTRODUCTION

The bonding in the metastable crystalline phase is generally described as “resonant” where further gain in energy is achieved due to the splitting of the six identical bonds into subsets of three shorter and three longer bonds, a concept usually referred to as Peierls distortion. Our experiments demonstrate that the distortion of the metastable phase does not disappear with temperature contrary to what one would expect for a Peierls-distorted structure but either decreases very slightly or even increases with temperature (Fig. 1).[1] At the same time, computer simulations show that the electron density does not resonate between the two adjacent bonds but remains concentrated along the shorter bond with the electron density along the longer bonds being much weaker [2], i.e. the structure is characterised by primary and secondary bonds and possesses a strong bonding energy hierarchy (Fig. 2). In such a case, a temperature increase destabilises the subsystem of the secondary bonds that determine the formation of the ordered phase eventually leading to the loss of long-range order.

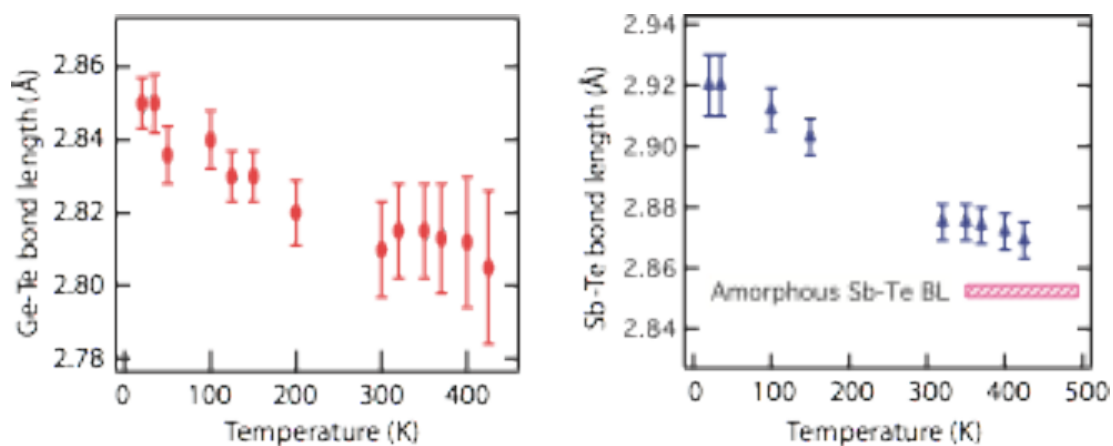


Figure 1: Variation of the shorter Ge-Te and Sb-Te bond lengths with temperature demonstrating that the system of the shorter primary bonds gets stronger while that of the secondary bonds gets weaker with temperature [2].

2. RESULTS & DISCUSSION

While in early publications the structure of the amorphous phase was tacitly assumed to be random. Recent experimental and computer studies have demonstrated that it has a rather well defined short-range order. One of the most controversial issues is the appropriateness of the Ge umbrella flip model suggested from EXAFS and XANES studies [2] since subsequent computer simulations [3-6] consistently found that the majority of Ge atoms preserve octahedral bonding angles. Our recent DFT simulations provided evidence that the so-called “four-fold coordinated Ge atoms with octahedral bonding angles” are in fact pyramids with Ge atoms located at the apex. Simulated XANES spectra of such building blocks together with those for tetrahedrally coordinated Ge sites are in very good agreement with experimental results [1].

These results allow us to suggest the following mechanism of amorphisation for composite Ge-Sb-Te alloys. Upon acquiring critical distortions leading to misalignment of the atoms - for example due to thermal vibrations - the secondary bonds, that are formed using back-lobes of the same orbitals that form primary bonds, break and the long-range order of the crystalline phases collapses [7] giving rise to the amorphous phase through rotation and distortion of GeTe_3 pyramids with the occasional formation of Ge-Ge bonds generating tetrahedrally coordinated Ge sites. These findings are in perfect agreement with the XANES simulation results.

While in GeTe that nominally does not contain vacancies, amorphisation without the umbrella flip seems to dominate, in GST alloys, the formation of tetrahedral Ge sites is quite likely since vacancies serve to stabilize the tetrahedral bonding geometry [8]. This process is especially likely in $\text{GeTe/Sb}_2\text{Te}_3$ layered structures where vacancies are spatially well defined and the atomic motion is limited to a single dimension [9].

Loss of the long-range order in solids with bonding energy hierarchy can be strongly influenced by electronic excitation when the creation of electrons in the antibonding states that form the bottom of the conduction band further weakens the secondary bonds. This effect has been demonstrated for various chalcogenide glasses when the amorphisation process has been shown to proceed without a significant temperature increase at temperature much lower than that of thermal melting [10,11]. Our recent in-situ XANES studies of sub-nanosecond pulse-induced amorphisation in Ge-Sb-Te demonstrate that this process also takes place without going through a conventional molten phase [12].

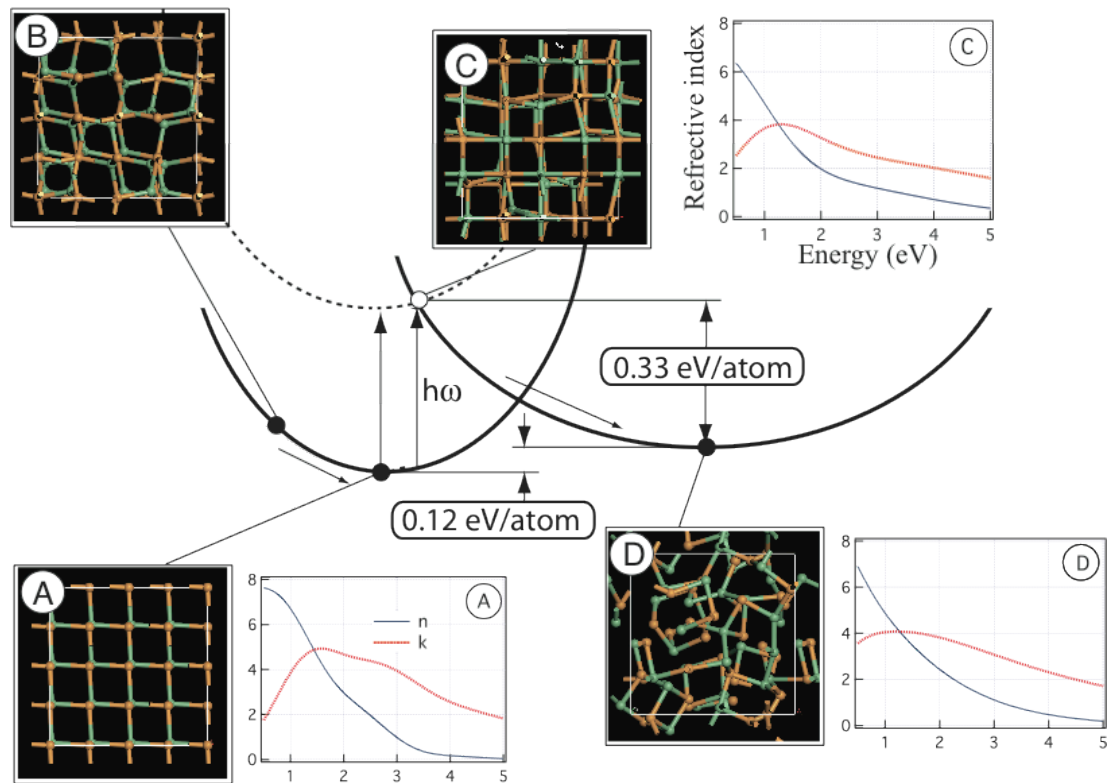


Figure 2: Strong energy hierarchy between the short and long bonds in the rhombohedral phase of GeTe [7]

3. CONCLUSION

Our results further show that the change in electronic properties takes place at an initial stage of the phase-change process when the secondary bonds are broken but the structure still retains - on the average - the long-range order of the crystalline cubic phase. This finding provides evidence that the electronic contrast between the two states is determined not by the existence, or lack, of the long-range order but by the character of bonding as was also suggested in [13].

REFERENCES

- [1] M. Krbal, A. Kolobov, P. Fons, J. Tominaga, S. Elliott, J. Hegedus, and T. Uruga. "Intrinsic complexity of the melt-quenched amorphous memory alloy $\text{Ge}_2\text{Sb}_2\text{Te}_5$ ", *Phys. Rev. B*, 83 (2011) 054203.
- [2] A. Kolobov, P. Fons, A. Frenkel, A. Ankudinov, J. Tominaga, and T. Uruga. "Understanding the phase-change mechanism of rewritable optical media", *Nature Mater.*, 3 (2004) 703.
- [3] J. Akola and R. Jones. "Density functional study of amorphous, liquid and crystalline : homopolar bonds and/or AB alternation?" *J. Phys. Cond. Mat.*, 20 (2008) 465103.
- [4] S. Caravati, M. Bernasconi, T. Kühne, M. Krack, and M. Parrinello. "Coexistence of tetrahedral-and octahedral-like sites in amorphous phase change materials". *Appl. Phys. Lett.*, 91 (2007) 171906.
- [5] J. Hegedüs and S. Elliott. "Microscopic origin of the fast crystallization ability of Ge–Sb–Te phase-change memory materials". *Nature Mater.*, 7 (2008) 399.
- [6] S. Kohara, K. Kato, S. Kimura, H. Tanaka, T. Usuki, K. Suzuya, H. Tanaka, Y. Moritomo, T. Matsunaga, N. Yamada, Y. Tanaka, H. Suematsu, and M. Takata. "Structural basis for the fast phase change of : Ring statistics analogy between the crystal and amorphous states". *Appl. Phys. Lett.*, 89 (2006) 201910.
- [7] A. V. Kolobov, M. Krbal, P. Fons, J. Tominaga, and T. Uruga. "Distortion-triggered loss of long-range order in solids with bonding energy hierarchy". *Nature Chem.*, 3 (2011) 311.

- [8] C. Lang, S. A. Song, D. N. Manh, and D. J. H. Cockayne. "Building blocks of amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ ". *Phys. Rev. B*, 76 (2007) 054101.
- [9] R.E. Simpson et al., Nature Nanotech, Advanced Online Publication, 03 July 2011.
- [10] A. Kolobov and S. Elliott. "Reversible photo-amorphization of a crystallized alloy $\text{As}_{50}\text{Se}_{50}$ ". *Philos. Mag.*, 71 (1995) 1.
- [11] P. Kolobov. "Photomelting of selenium at low temperature". *Appl. Phys. Lett.*, 74 (1999) 215.
- [12] P. Fons, H. Osawa, A. V. Kolobov, T. Fukaya, M. Suzuki, T. Uruga, N. Kawamura, H. Tanida, and J. Tominaga. "Photoassisted amorphization of the phase-change memory alloy $\text{Ge}_2\text{Sb}_2\text{Te}_5$ ". *Phys. Rev. B*, 82 (2010) 041203.
- [13] B. Huang and J. Robertson. "Bonding origin of optical contrast in phase-change memory materials". *Phys. Rev. B*, 81 (2010) 081204R.

Biography

AK started his activities in the field of chalcogenides in 1979 when he joined the laboratory headed by Prof. B.T. Kolomiets, the father of amorphous semiconductors at the Ioffe Institute. He has worked at Cambridge University, Ecole superieure de physique et de chimie industrielles de la ville de Paris, and Katholieke Univesiteit Leuven before joining AIST (Tsukuba) in 1994. At present he is prime senior researcher at the Nanoelectronics Research Institute.