

Phase Change Materials and Superlattices for Non-Volatile Memories

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The global size of data doubles every two years and will reach 44 zettabytes by 2020. Such huge amount of data poses a serious challenge on data storage and processing. To further improve computing and power efficiencies, changes in computing architecture and hardware are urgently needed. Chalcogenide phase-change material based random access memories (PRAMs) are one of the leading candidates for such purpose. PRAMs combine the advantages of non-volatility and fast operation speed, and they have recently entered the global memory market as Storage-Class Memories (SCMs), filling the performance gap between dynamic random access memories (DRAMs) and flash memory-based solid state hard drives (SSDs). In addition, PRAMs hold the promise for subnanosecond memory operations and neuro-inspired computing, which may lead to the development of universal memory and brain-like computing devices. These novel devices are expected to result in a substantial improvement in computing and power efficiencies, owing to the fundamental change in memory hierarchy and computing architecture.^[1]

The working principle of PRAMs is to exploit the large contrast in electrical resistance between the amorphous state and crystalline state of phase-change materials (PCMs). The switching of PRAMs is accomplished by the rapid and reversible crystallization (SET) and melt-quenched amorphization (RE-SET) of PCMs under electrical pulses (via Joule heating). Most PCMs can be located in the ternary Ge–Sb–Te diagram, including the $(\text{GeTe})_m(\text{Sb}_2\text{Te}_3)_n$ compounds, alloyed Sb_2Te and alloyed Sb compounds. The most frequently studied and commercially employed PCM is $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST). Recently, $(\text{GeTe})_m(\text{Sb}_2\text{Te}_3)_n$ alloys are made into superlattices, and are designed to employ reversible transitions within the crystalline states for low-power memory operations. Such new type of memory devices is named as interfacial phase-change memories (iPCMs). The detailed switching mechanisms of PRAMs and iPCMs are under active investigations. In this Focus Issue, we

present six review articles and five research letters to cover various aspects of PCMs, including studies on crystallization kinetics, resistance drift, structural characterizations, superlattice switching, disorder-induced electron localization, chemical bonding properties, high-pressure behaviors as well as progress in device fabrications and chip integrations.

Ab initio simulations

Ider Ronneberger et al.^[2] performed AIMD simulations to access the crystallization properties of Sb, $\text{In}_{15}\text{Sb}_{85}$ and $\text{Ge}_{15}\text{Sb}_{85}$. Unalloyed Sb is shown to be extremely prone to crystallization, while In atoms partly and Ge atoms largely slow down the crystallization kinetics of Sb. This trend in crystallization speed is in line with previous experimental observations. The detailed mechanism is explained by the increasing structural deviation of In- and Ge-based local motifs with respect to the pure Sb amorphous network.

Jean-Yves Raty^[3] presents an overview of recent theoretical efforts on understanding the aging process in amorphous GeTe. Aging is responsible for the resistance drift phenomenon that hinders the implementation of multi-level data storage in PRAMs. The timescale of aging varies by several orders of magnitudes and is inaccessible by regular AIMD simulations. Advanced simulation techniques that were used to generate aged amorphous models, such as chemical substitution, metadynamics and Monte-Carlo like methods, are discussed in detail.

Philipp Konze et al.^[4] focused on the chemical-bonding properties of PCMs. The bonding analyses reviewed in this article were primarily made by the crystal orbital Hamilton population (COHP) method. Such orbital-based bonding indicators shed light on a couple of important questions in complex crystalline phase and even amorphous phase of PCMs. In addition, chemical-bonding analyses also assist the design of Sc–Sb–Te compounds, which enables subnanosecond switching of conventional PRAM devices.

Experiments and devices

Matthias Dück et al.^[5] report an electrical transport study of crystalline GeSb_2Te_4 . In this work, ~ 10 nm thin films were deposited on heated substrates, which enabled the growth of samples with similar lateral grain size but different levels of lattice disorder. The transport measurements revealed that with little changes in grain size, the electron mean free path in crystalline GeSb_2Te_4 samples can be altered by a factor of 20. This observation confirmed that the metal–insulator transition in crystalline GeSb_2Te_4 is governed by intra-grain lattice disorder, not by grain boundary scattering.

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Francesco Di Biagio et al.^[6] studied the crystallization properties of Ge-rich compounds along the GeTe–Sb₂Te₃ pseudo-binary line. For these compounds, e.g. Ge₁₀Sb₂Te₁₃, the amorphous films crystallize in the GeSb₂Te₄ composition with large amounts of Ge nanocrystals. If a two-step annealing procedure is employed, i.e. an incubation step at lower temperature (180 °C was used) and an annealing step for crystallization (270 °C), the concentration of crystalline Ge can be reduced effectively, paving the way for the control of the microstructure and electrical/thermal properties of Ge-rich alloys.

Kailiang Xu et al.^[7] present an overview on the high-pressure behaviors of PCMs. In addition to temperature, pressure serves as another important thermodynamic parameter to tailor the materials properties and trigger phase transitions in PCMs. Multiple structural transitions as well as changes in electronic structure and bonding properties of GST under pressure are discussed in detail. A brief summary on the high-pressure behaviors of Sb₂Te₃ and GeSe for applications in topological insulators, thermoelectrics and memory selectors is also provided.

Xi Li et al.^[8] present an overview on phase-change memory for embedded applications. With carbon-doped GST and improvements in device fabrications, circuits design as well as operation algorithms, they have demonstrated a 128 Mb embedded chip in 40 nm node. The chip could operate with a minimum programming time of 200 ns over 10⁹ SET/RESET cycles and with good data retention. The estimated 10-year retention temperature is 128 °C. In addition, recent progress on materials synthesis and optimization for DRAM-like applications is also reviewed.

Superlattices

Junji Tominaga^[9] reviewed the development on iPCM. The central idea of turning GST into GeTe/Sb₂Te₃ superlattices is to reduce the energy loss during crystal–liquid–amorphous transitions, having reversible transitions within crystalline states without melting. Several recent experiments supporting this switching mechanism, in particular the observation of a special ferroelectric state, are reviewed. Although further verification on the switching mechanism is required, the iPCM studies have unexpectedly initiated the development of spintronics in GeTe/Sb₂Te₃ superlattices that is related to some topologically nontrivial states.

Bart Kooi and Jamo Momand^[10] present an overview on structural characterizations of superlattices using (scanning) transmission electron microscopy ((S)TEM). Such technique provides direct real-space structural information in nano- and atomic-scale, serving as a powerful tool to identify various crystalline structures and defects for potential iPCM switching. Critical remarks about the switching mechanisms, such as the quest for Ge–Ge bonds, GST formation and intermixing, the role of bilayer defects and strain effects, were thoroughly reviewed. Future research directions on chalcogenide superlattices are proposed.

Mattia Boniardi et al.^[11] report an experimental work on GeTe/Sb₂Te₃ superlattice-based memory devices. A GeTe/Sb₂Te₃ superlattice was grown by molecular beam epitaxy, which however, ended up with a GeSb₂Te₄/Sb₂Te₃ superlattice. Memory devices based on this superlattice film were tested thoroughly, which showed a significant reduction in both SET and RESET currents. The electrical responses, in particular a threshold switching in the RESET state, of this superlattice memory cell were found similar to the standard GST memory cell. Therefore, a partial thermal-based transition mechanism is proposed.

Henning Hollermann et al.^[12] explored the potential of stoichiometry determination for chalcogenide superlattices via X-ray diffraction (XRD). Kinematic scattering theory was employed to link the average composition with the diffraction features. The observed lattice constants of the (GeTe)_x(Sb₂Te₃)_{1–x} superlattices reference unit cell follow Vegard's law, enabling a fast and non-destructive stoichiometry determination. This simplified model provides a reasonable estimate despite the presence of intermixing near the interfaces.

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