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Phase-Change and Ovonic Materials (Second Edition)

Pierre Noé, Bart J. Kooi, and Matthias Wuttig*

It is our great pleasure to introduce this second edition of the focus issue on phase-change and ovonic materials. This special issue aims to summarize recent progress in the rapidly developing field of phase-change and ovonic materials and their numerous applications. It provides a snapshot of the state-of-the-art, both experimental and theoretical, for both experienced and young researchers interested in this subject area. Since its very first edition in 2019, we expect to publish this issue yearly within the framework of the European Phase-Change and Ovonic Symposium (E\PCOS). E\PCOS was born in Switzerland in 2001, with the aim of providing a platform to discuss and promote the basic science of phase-change materials (PCMs). This goal also included their applications in rewritable optical disks, which were at that time commercialized as CDs. Later on, also DVD and Blu-ray disk formats were successfully developed and lastly in 2017 nonvolatile phase-change memories were introduced in the market, defining a further milestone. E\PCOS had grown out of the first symposium on Phase-Change and Optical Storage technology (PCOS) based in Japan in 1990, thanks to Professor Masahiro Okuda, who was the advisor of E\PCOS from its beginning. In recent years, the field has diversified tremendously. While the scientific and technological footprints of the founding father of the field, the late Stanford Ovshinsky, are still clearly visible, the number of topics addressed has increased significantly.

To date, E\PCOS has become the leading international conference on this exciting and still very dynamic topic. However, in 2020 the worldwide COVID-19 crisis constrained the E\PCOS program committee to cancel for the very first time a meeting that was supposed to be held at Oxford as usual early September. Therefore, this 2020 focus issue sounds unprecedented and special for all of us. By showcasing the latest results as well as outlining the ongoing challenges that can be raised by the active E\PCOS community, we hope that it will help to maintain the strong link and the tremendous exciting scientific debates between main actors and players in the field, from both academic and industry, waiting hopefully for better days.

Besides, this second focus issue will mark the history of the E\PCOS with an exciting large number of papers to be published, covering a rich variety of topics beyond phase-change memories. This is well illustrated through the review paper on PCM and devices physics from Yanyun Ren et al. (article number **2000394**), showing the promising features of PCM for neuromorphic applications, as well as in the paper from Minh Anh Luong et al. (article number **2000471**), describing some unique features of uncommon Ge-Rich GeSbTe PCM alloys to be compatible with high-temperature environments as those experienced by nonvolatile embedded phase-change memories. In addition, Minh Anh Luong et al. (article number **2000443**) provide more details on the impact of nitrogen on the crystallization and microstructure of such amazing Ge-Rich GeSbTe alloys.

A journey through this 2020 special issue emphasizes once again, despite their present wide use in many daily applications, that the underlying physical mechanisms at origin of the unique properties portfolio of phase-change materials (PCM) provide unique opportunities to advance our understanding of materials and their applications. Understanding the bonding in PCMs has been seen as an opportunity to unravel the origin of the unconventional properties of crystalline PCMs. Tae Hoon Lee et al. (article number **2000516**) pursue this approach and conclude that multicenter hyperbonding, i.e., an electron configuration where three atoms are held together by four electrons (3c/4e) provides a straightforward explanation of the striking material properties, such as the high Born effective charges or the large contrast between the amorphous and crystalline phase. A similar goal has also motivated the work presented by Yudong Cheng et al. (article number **2000482**). Yet, these authors invoke a different bonding mechanism, where about one electron is located between adjacent atoms. They make another step forward and present a map that identifies those materials that employ this bonding mechanism and separate it from the well-known textbook cases of ionic, metallic, and covalent bonding. Molecular dynamic simulations and electronic structure analyses based on density functional theory (DFT) are used by Nian-Ke Chen et al. (article number **2000441**) to study the formation of crystal nuclei in the amorphous matrix for $Ge_2Sb_2Te_5$ (GST). This provides further insights in the atomic movements, the evolution of basic motifs and electronic properties during crystal nucleation in GST. Yu-Xing Zhou et al. (article number **2000403**) promote another recent development, the use of machine learning to advance simulations of supercooled liquid PCMs, focusing on GST. They demonstrate the potential of this approach by showing superior length and time scales compared

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to molecular-dynamics-based DFT calculations. The same approach is also utilized by Felix Mocanu et al. (article number **2000485**), who study the chemical bonding of amorphous Sb_2Te_3. The determination of the atomic arrangement and the classification of the electronic states in the vicinity of the Fermi level enables them to link material properties and crystallization kinetics. The atomic arrangement in amorphous networks is also the topic of a paper by Matthieu Micoulaut et al. (article number **2000490**), who study $GeTe_2$ and find evidence for tetrahedrally bonded motifs, revisiting a vivid debate that has shaped the community in the last decade, when competing models for amorphous phase-change materials were presented and discussed. A novel phase-change compound is discussed by Dario Baratella et al. (article number **2000382**), who study crystalline $Ga_4Sb_6Te_3$ and reveal its octahedral coordination, combining electronic structure calculations with a genetic algorithm. Computing Raman spectra for different atomic environments, they offer a pathway to discriminate among the different possible atomic arrangements. By combining DFT and Raman spectroscopy, a direct and simple nondestructive method is demonstrated by Eugenio Zallo et al. (article number **2000434**) to quantify the number of "van der Waals" lamellae in epitaxially grown GeSbTe films, highlighting the advantage of the MBE growth technique for precisely controlling film thickness. Jean-Pierre Gaspard (article number **2000536**) focuses on another facet of phase-change materials, their anharmonic properties. He concludes that a simple interatomic potential can explain the unconventional vibrational properties of crystalline PCMs, including their large Grüneisen parameter for transverse optical modes, which leads to a low thermal conductivity, a prerequisite for energy efficiency.

For experimental characterization of PCMs the major platform remains thin films. Koichi Shimakawa et al. (article number **2000411**) show that grain boundaries significantly affect the THz and DC conductivities of crystalline (distorted rock-salt structure) GST for temperatures >300 K, suggesting that intra- and intergrain transport mechanisms jointly control the electronic transport in these materials. Magnetic phase-change behavior is studied by Chao He et al. (article number **2000425**), showing that an amorphous film of $Fe_{48}Mo_{14}Cr_{15}C_{15}B_6Y_2$ exhibits spin-glass behavior, whereas the crystalline film is ferromagnetic, rendering this material suitable as a magnetic phase-change material. Martina Tomelleri et al. (article number **2000451**) show exciting results on $GeSe_{1-x}Te_x$ thin films. GeSe is not useful as a PCM, but by replacing at least 1/6 of the Se atoms with Te atoms, it becomes a PCM with unprecedented large resistivity contrast and very high thermal stability (up to 10 years at 272 °C) for an alloy without significant phase separation upon crystallization, making it highly promising for high-temperature automotive and embedded applications. Although being an important parameter for characterizing PCMs, the glass transition temperatures T_g of PCMs generally remains elusive, because it is obscured by crystallization. Julian Pries et al. (article number **2000478**) show a new approach to assess the T_g of GeTe by selective crystallization of pure Te during sub-T_g annealing of $Ge_{15}Te_{85}$, leading to a gradual change in composition of the amorphous surroundings, toward that of GeTe.

A significant number of papers is also devoted to device physics. Yi Shuang et al. (article number **2000415**) studied the transport mechanisms in amorphous and crystalline nitrogen-doped $Cr_2Ge_2Te_6$ in detail, providing better understanding of its unusual phase-change behavior, with large resistance contrast not generated in the bulk, rather only at the interface with the tungsten electrodes. Alin Velea et al. (article number **2000475**) describe multilevel memristive GeTe devices, in which they realize a significant number of intermediate resistivity values. Using a space-charge-limited conduction model they can reproduce and explain the measured transport properties. Mozhikunnam Sreekrishnan Arjunan et al. (article number **2000354**) focus on a less studied material, In_3SbTe_2. They show the high-stability and low-noise multilevel switching in this material by employing laser pulses of just 5 ns. Besides, exploring the devices physics could open further opportunities for memory applications. For instance, Nadim Kanan et al. (article number **2000422**) propose an innovative programming strategy such as thermal cross-talk in phase-change devices for use as a coupling mechanism to achieve logic functions that could decrease the complementary metal–oxide–semiconductor (CMOS) footprint necessary for high-density PCM arrays. Further improvement of the reliability of PCM memories is still a challenge and is under the scope of the paper of Hwanwook Lee et al. (article number **2000419**), in which they investigate the stuck reset failure in memory devices by means of finite element simulation of the phase-change stress. In the same context, among all the challenges to be faced by PCM memory technology, a major one deals with the reduction of the programming energy required to switch the PCM between its two different resistance states. To this aim, optimizing the device architecture has, up to now, been the main approach in PCM technology in order to increase the thermal resistance and hence the Joule heating efficiency within the memory cell upon programming pulses. By using a similar approach, Shogo Hatayama et al. (article number **2000392**) go one-step beyond by coupling a new PCM alloy, namely $Cr_2Ge_2Te_6$, with innovative electrode materials. Indeed, they propose that using a LaB_6 electrode instead of the commonly used W one permits significant increase of the contact resistivity, hence reducing the total operation energy of the LaB_6 PCM device. Similarly, Damien Térébénec et al. (article number **2000538**) demonstrate the successful integration of highly oriented $[(GeTe)_2/(Sb_2Te_3)_m]_n$ superlattices (SLs) in a memory device. By means of scanning transmission electron microscopy imaging of a memory cell, they unambiguously show, for the first time, that such SL-based devices can switch to the RESET state following the same melting–quenching mechanism than in memory devices using standard polycrystalline PCM alloys, i.e., through the local amorphization of the SL. The RESET current is significantly lower in SL-based devices and is further improved upon increasing the m value from 2 to 8, m corresponds to the number of Sb_2Te_3 quintuple layers (QLs) of about 1 nm each. This improvement could result from a better cross-plane thermal confinement within the SLs with an important role played by stacking defects such as bilayer ones. Such SLs, as well as devices based on the latter, sometimes called iPCMs (for interfacial phase-change memories), are also under the attention of a significant number of papers. The longstanding and active debate on the physical processes that are behind improvement

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of SL-based devices performance and switching mechanism is again widely investigated. Hisao Nakamura (article number **2000393**) studied the change of thermoelectric and phonon thermal properties of an iPCM device by first-principles transport calculations based on theoretical $(GeTe/)_2/Sb_2Te_3$ atomic models. The simulated SL models consisted of a stacking of pure Ge, Sb, and Te atomic planes with three different types of cation layers exchange. Again using $(GeTe/)_2/Sb_2Te_3$ atomistic models containing pure Ge, Sb, and Te atomic planes, Paul Fons et al. (article number **2000412**) performed ab initio molecular dynamics simulations to explore electric field effects on proposed iPCM structures. Unlike previous speculation in the literature, the effect of electrical fields on Ge atoms is shown to be negligible and, rather, to strongly affect the van der Waals gaps between the Te atoms. Therefore, these new insights further call for a deep revision of iPCMs models and the related switching mechanism. By using ab initio molecular dynamics simulations, Valentin Evang et al. (article number **20000457**) explore an alternative switching mechanism for SL devices based on amorphous–crystalline transitions of ultrathin GeSbTe layers between crystalline Sb_2Te_3 QLs. The growth of such promising $(GeTe/)_2/Sb_2Te_3$ SLs was made possible on various substrates only thanks to the 2D behavior of the layered Sb_2Te_3 material. It has to be emphasized that Sb_2Te_3 is also a case of study for its unique topological electronic properties, since it is considered as a prototypical topological insulator (TI). This is the TI property of Sb_2Te_3 crystalline structure that Alexander Kolobov et al. (article number **2000418**) explore by means of ab initio simulations in order to study the disappearance of the so-called Dirac cones along certain crystal side surfaces. The Dirac cones are at origin of the TI properties and correspond to surface states characterized by metallic states with linear dispersion. Finally, Yuta Saito et al. (article number **2000414**) study the growth of new stacking sequences using 2D Bi–Te layered compounds to replace the Sb–Te ones to move from the most widely studied Ge–Sb–Te SLs toward innovative Ge–Bi–Te SLs. Moreover, they investigate the potential topological properties of successfully grown BiTe/SbTe heterostructures by means of DFT-based calculations for the purpose of future achievement of novel functional devices.

To conclude, we hope you will enjoy this 2020 "grand cru" showing the latest research on phase-change and ovonic materials. We also wish that this issue will provide a unique opportunity to keep the link between us waiting for the next E\PCOS meeting that is planned for September 2021. Despite large-scale vaccination programs having started, organizing a regular meeting in Oxford is currently still considered too risky. Postponing E\PCOS for another year is also not an option and therefore an online meeting is in preparation. Although this is not our dreamed scenario, let us hope that a very lively and exciting conference will be made possible, also celebrating our 20 years anniversary of E\PCOS, and that it may be the start of a next decade in which phase-change materials and its research will prosper, where we can come together at inspiring venues, keeping our community as active as during the last two decades with its usual exciting lively discussions.

Pierre Noé, Bart J. Kooi, and Matthias Wuttig
Guest Editors

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phase-change materials, ovonics, chalcogenides, EPCOS

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Guest Editors Biographies

Pierre Noé joined the basic research department of CEA in 2000 as a materials engineer to work on Si-based nanostructured materials for microelectronics, photonics and spintronics (CEA-DRFMC then CEA-INAC after 2008, Grenoble, France). In 2011, he became a permanent researcher at CEA-Leti and received a Ph.D. degree in physics in 2013 from Grenoble-Alpes University. Since then he started his own research group on Advanced Chalcogenide Materials within the Silicon Technologies division of Leti. His main research interest focuses on elaboration and materials science investigations of innovative chalcogenides at the frontier between basic knowledge and technological applications (memories, photonics, thermoelectricity...).

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Bart J. Kooi obtained his Ph.D. degree in materials science in 1995 from Delft University of Technology, Netherlands. Since then, he has worked at the University of Groningen (The Netherlands) as assistant, associate, and full professor, starting his own research group, Nanostructured Materials and Interfaces, within the Zernike Institute for Advanced Materials in 2009. His main research interests are nanostructure–property relations, advanced transmission electron microscopy, interfaces, phase transformations, and tellurium- and antimony-based materials for thermoelectric and phase-change memory applications.

Matthias Wuttig received his Ph.D. in physics in 1988 from RWTH Aachen/Forschungszentrum Jülich. He was a visiting professor at several institutions including Lawrence Berkeley Laboratory, CINaM (Marseille), Stanford University, Hangzhou University, IBM Almaden, Bell Labs, DSI in Singapore, and the Chinese Academy of Sciences in Shanghai. In 1997, he was appointed Full Professor at RWTH Aachen. Since 2011, he has been heading a collaborative research center on resistively switching chalcogenides (SFB 917), funded by the German Science Foundation (DFG).

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