Emerging phase-change memory, a new type of nonvolatile random-access memory, promises faster, denser, and reliable data storage that could replace the current flash memories (1). The application of a phase-change material in such devices takes advantage of the reversible switch and the large property difference between two contrasting (amorphous and crystalline) states. A prototypical phase-change material already used in random-access memories is the chalcogenide Ge2Sb2Te5 alloy (GST225, abbreviated as GST). Upon crystallization at around 420 K from fully amorphous GST (α-GST) to crystalline rock-salt GST (ρs-GST), the electrical resistivity drops by at least two orders of magnitude, offering the desired contrast for memory applications. This scenario is shown in Fig. P1A, which is adapted from ref. 2.

Instead of using the thermodynamic variable of temperature to induce phase transition and resistivity contrast, we have probed the structure and property changes in α-GST, entirely in the amorphous state, as a function of the other thermodynamic variable, “pressure” (P). Pressure and stresses are usually present in devices, and GST exhibits rich behavior in phase transformations under pressure (3, 4). For example, ρs-GST loses its long-range order (which enables the translational symmetry of crystal lattices) and turns amorphous at P ≈ 15–20 GPa, which eventually crystallizes into a body-centered-cubic (bcc) crystalline phase at P ≈ 28 GPa. On the other hand, α-GST remains fully amorphous from ambient pressure up to approximately 28 GPa, before crystallization into the bcc crystal. The property variation of this amorphous chalcogenide over such a wide pressure regime (0 to approximately 28 GPa) and the corresponding evolution of local structure still remain a mystery and are thus the focus of this work. Our discovery here is a dramatic decrease in electrical resistivity under pressure, by as much as four orders of magnitude, in glassy α-GST in the absence of crystallization. We also shed light on the underlying mechanism of this decrease in resistivity by revealing the local structural evolution responsible for the property variation and its effects on energy band structure and electrical conductivity of α-GST.

The α-GST samples were subjected to nominally hydrostatic pressure of up to 33 GPa in a diamond anvil cell—a device that permits compression of a piece of material to extreme pressures—along with in situ X-ray diffraction and in situ electrical resistivity measurements. The detailed atomic structure was modeled by ab initio molecular dynamics simulations.

In Fig. P1B, we have plotted the electrical resistivity with increasing pressure of up to 20 GPa. Interestingly, the

![Fig. P1. (A) Electrical resistivity of GeSb2Te5 as a function of temperature, adapted from ref. 2. The amorphous-to-crystalline transition occurs at around 420 K, with a resistivity drop by about two orders of magnitude. The ab initio models of these two structural configurations are displayed in the Insets. (B) Electrical resistivity of amorphous Ge2Sb2Te5 (α-GST) with increasing pressure. The representative local motifs in the amorphous structure are shown schematically in the Insets: The LED regions are compressed first as the electrical resistivity decreases by about four orders of magnitude in the lower pressure regime (0–8 GPa), after which the characteristic bond angle starts to be compressed to decrease from around 90° to approximately 55°, and the low-pressure rock-salt-type α-GST (ρs-type α-GST) gradually transforms into a high-pressure body-centered-cubic-type polymorph (bcc-type α-GST), before eventually crystallizing into the bcc GST at 28 GPa.](image-url)
The resistivity of a-GST was found to experience a precipitous drop in the pressure regime of \( P = 0 \text{–} 8 \text{ GPa} \). Such a decrease in the electrical resistivity by about four orders of magnitude is comparable to the potential range achievable by thermal-annealing-induced phase transitions (Fig. P1A) and in fact more pronounced than that in the abrupt phase transition of a-GST to rs-GST used in current memory devices. This dramatic property change is found to be accompanied by subtle changes in the parameters normally used to describe and monitor local structure, such as bond length, bond angle, and coordination number. Instead, we discovered an important structural indicator that changes fast with increasing pressure and correlates strongly with the resistivity change: the volume fraction of low-electron-density (LED) regions, which are “vacant” local volumes analogous to voids or vacancies in crystalline materials (5). The local motifs and LED regions are shown schematically in the insets of Fig. P1B. The obvious decrease in LED volumes resulting from electron charge density redistribution under increasing pressure offers a useful structural signature that can be monitored to represent all the important changes in the atomic structure and bonding that mediate significant property variations. Our ab initio calculation suggests that the pressure-driven compression of the LED volumes in a-GST narrows the band gap by enhancing the interactions between local clusters. We also used electron localization functions, which measure the degree of the localization of electrons and thus reflect the nature of bonds, to provide evidence that at elevated pressures, some originally trapped electrons become less localized. These observations suggest that it is the narrowing of the mobility gap (the energy gap between extended conduction and valence bands in glasses, analogue to the band gap in crystals) under pressure that results in the pronounced increase in conductivity.

With the pressure increased to greater than 8 GPa, the electrical resistivity levels off, approaching a plateau, as shown in Fig. P1B. The resistivity value is now close to the high-end value for metals. An interesting finding in addition to the property change is an obvious evolution of the atomic structure in this pressure regime, as illustrated by schematic insets in Fig. P1B. Different from the lower pressure regime (0–8 GPa), where a-GST largely retains its right-angled local motifs (i.e., those with bond angles of around 90°) that bear some resemblance to the low-pressure crystalline form (rs-GST), at \( P > 8 \text{ GPa} \), when most of the LED regions have already been squeezed down, the bond angles start to be compressed. The glass eventually transforms to a different amorphous state, characterized by a bond angle distribution starting at around 55° and coordination numbers approaching 8. This local configuration is thus very different from the low-pressure one and bears similarity to the local structure of the high-pressure (approximately 28 GPa) crystallization product, a bcc GST. As such, this high-density, metallic-like a-GST can be identified as a bcc-type polyamorph (a material capable of existing in various amorphous forms) and regarded as a precursor of the eventual bcc GST upon high-pressure crystallization.

2. Siegrist T, et al. (2011) Disorder-induced localization in crystalline phase-change mate-
5. Sun ZM, et al. (2011) Pressure-induced reversible amorphization and an amorphous-