Local instability of *p*-type bonding makes amorphous GeTe a lone-pair semiconductor

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Bonding in the crystalline phase of GeTe-based phase-change alloys is believed to be purely *p* type. In this work we demonstrate that in the absence of long-range order, despite the preserved bonding angles of $\sim 90°$, sp^3 hybridization is more favorable with a pair of nonbonding electrons localized on a Ge sp^3 orbital, i.e., in contrast to the crystalline phase, amorphous GeTe is a lone-pair (LP) semiconductor. Upon disordering, tetrahedral Ge sites are formed due to unpairing of LP electrons and subsequent formation of additional Ge-Ge bonds, a process generating additional free electrons. Recombination of these electrons during the structure relaxation may be the underlying reason for the conductivity drift in the amorphous phase making the latter process analogous to persistent photoconductivity. Implications for the stability of the amorphous phase are also discussed.

Tellurium-based alloys along the GeTe-Sb$_2$Te$_3$ (GST) tie-line are widely used in optical memory devices such as digital versatile discs and also in recently commercialized phase-change random-access memory (PC-RAM). In these materials, information is stored as optical and/or electrical property contrast arising from structural differences between the crystalline and amorphous phases.[1] Despite significant progress on the application front, many fundamental issues still pose important challenges.[2]

Chalcogenides such as sulfur and/or selenium, that are typical lone-pair semiconductors,[3] are known to form layered structures with covalentlike interaction within layers where chalcogen species are twofold coordinated. For GeTe-based memory alloys, on the other hand, Bragg diffraction studies suggested the device-relevant metastable crystalline phase of GST has the rocksalt structure with Te atoms forming one face-centered-cubic sublattice and Ge/Sb and vacancies forming the other.[4] Subsequent extended x-ray absorption fine structure (EXAFS) experiments demonstrated that locally the structure is distorted similar to the case of binary GeTe and has subsets of three short (~ 2.83 Å) and three long Ge-Te (~ 3.15 Å) interatomic distances, i.e., are locally 3 + 3 coordinated.[5]

The formation of a rocksaltlike structure requires each of the constituent elements to possess six valence electrons. Since Ge (group IV) and Sb (group V) have less than six electrons, purely covalent bonding is not possible. To account for this controversy, the concept of resonant bonding in IV–VI semiconductors has been suggested.[6] Later, it was demonstrated that the resonant bonding plays an important role in determining the properties of the crystalline phase of GeTe-based phase-change alloys.[7] The present consensus is that bonding in these materials is *p*-type resonant and a slight difference between the shorter and longer bonds is due to a Peierls distortion. To account for the difference in bonding along the three shorter and three longer Ge-Te interatomic distances, the coordination in GeTe is often described as 3 + 3.

As an example of a material with such bonds, a group-V element antimony has been considered. Each Sb atom possesses three unpaired electrons on each of its three *p* orbitals and can thus form three covalent bonds with a bonding angle of 90°. Since Ge atoms are usually sp^3 hybridized, pure *p*-type bonding and octahedral bonding angles are not *a priori* expected. Especially so, because other chalcogens form crystals with GeS(e)$_2$ stoichiometry, where the coordination numbers for both species are in agreement with their location in the periodic table.

An explanation for this kind of bonding in GeTe-based alloys has been provided in terms of the formation of dative bonds utilizing Te lone-pair electrons in combination with the empty *p* orbitals of Ge atoms. The formation of such bonds, in addition to two conventional covalent Ge-Te bonds explains the *p* bonding in the crystalline phase of GeTe-based alloys, which can be considered analogous to antimony. Once formed, the dative bonds are indistinguishable from conventional covalent bonds.[8–10]

In the amorphus phase, bonding between the atoms is purely covalent with Ge atoms having two distinct local geometries. About two-thirds of the Ge atoms preserve threefold coordination and bonding angles close to 90° with the local atomic structure being rather similar to that in the crystalline phase.[11–13] In the literature such atoms are referred to as "defective octahedral sites" or "pyramidal" sites. At the same time, one-third of Ge atoms acquire tetrahedral bonding geometry with four equidistant first-nearest neighbors and bonding angles close to 109°. The coexistence of the pyramidal and tetrahedral sites has been confirmed by both *ab initio* simulations and experiments.[9] It was also found that certain atoms in the amorphous structure formed square-ring[13] or cubic[12] fragments that are very similar to atomic arrangement in the crystalline phase.

A question arises as to how the tetrahedral sites are formed and what is the driving force for their formation. Based on the results of x-ray absorption near-edge spectra (XANES) measurements, the present authors previously suggested[5] that the tetrahedral geometry is acquired though an umbrella flip of Ge atoms from an octahedral to a tetrahedral symmetry site within the Te fcc lattice. This model accounted for the observed changes in the bond lengths between the two phases but stayed short of considering the bond switching beyond the central Ge atom. Some subsequent studies challenged the possibility of the umbrella flip and it was speculated that the tetrahedral geometry could be acquired when two Ge atoms approach each

other during the relaxation process and an additional Ge-Ge bond is formed.[14] An important issue of how the electrons are redistributed when additional bonds are formed has not been addressed so far.

In this work, we first show using density functional theory (DFT) simulations for a GeTe case example that, upon amorphization, tetrahedral Ge sites form as a result of the rotation of cubic fragments with subsequent formation of Ge-Ge bonds. For an eight-atom GeTe cubic cluster that represents the simplest closed structure with 90° bonding angles and also argued to be a precurser for nucleation, we demonstrate that despite the bonding angles of $\sim 90°$ in GeTe, Ge species are sp^3 hybridized in nonperiodic structures. We propose that the local instability of p bonding drives structural relaxation upon loss of long-range order towards the formation of tetrahedrally located Ge species which, in particular, may account for the conductivity drift,[15] a phenomemon critical for industrial use of PC-RAM. At the same time, the formation of Ge-Ge bonds increases the stability of the amorphous phase, the parameter of utmost importance.

Density functional calculations were carried out on a 64-atom cell using the plane-wave code CASTEP.[16,17] Ultrasoft pseudopotentials were used for Ge, Sb, and Te atoms. The Ge and Te pseudopotential included the Ge $4s^2 4p^2$ and the Te $5s^2 5p^4$, as valence electrons, respectively. The exchange term was evaluated using the local density approximation from the numerical results of Ceperley and Alder[18] as parametrized by Perdew and Zunger.[19] The charge density was calculated with a plane-wave cutoff of 220 eV and a $2 \times 2 \times 2$ Monkhorst-Pack grid. For the relaxation processes the Broyden, Fletcher, Goldfarb, and Shannon algorithm[20] was used to relax the atomic coordinates at 0 K within a supercell of fixed volume; the volume was fixed to reflect the experimental determined density as conventionally done in the literature.

In a previous work, we have demonstrated that certain distortions introduced into the cubic phase of GeTe lead to its disordering. In particular, as described in Ref. 21, when the crystalline phase is distorted in such a way that resonant binding is preserved, e.g., by displacing Ge atoms along the $\langle 111 \rangle$ directions, the structure reverts to the ordered phase. At the same time, if the resonance bonding is broken, e.g., by making the shorter Ge-Te distances equal to the value charactersitic of the amorphous phase and misaligning the covalently bonded Ge-Te pairs, structural relaxation leads to a loss of long-range order. We have subsequently examined atomic trajectories for atoms acquiring tetrahedral bonding geometry in the latter case as a result of the relaxation. The results are shown in Fig. 1, where a fragment of the simulation cell that contains a tetrahedral site is shown. Frame 1 shows the distorted GeTe structure that becomes destabilized and relaxes to an amorphous phase. In frame 2 small rotations of the cubic fragments corresponding to the initial stage of the amorphization process are shown. As two Ge atoms approach each other, an additional Ge-Ge bond is formed, while the cubic fragments still maintain 90° bonding angles (frame 3). Finally, the structure relaxes to form tetrahedrally coordinated Ge atoms (frame 4).

This result has two important implications. The first one is that while in an ordered phase with long-range forces the cubic structure with 3 + 3 local coordination has minimum energy,

locally, i.e., in the absence of long-range forces, a structure with tetrahedrally coordinated Ge atoms is energetically more favorable than a structure that only contains pyramidal Ge sites. The second implication is that the tetrahedral bonding geometry of Ge atoms in the amorphous phase may be achieved without the umbrella flip proposed earlier. At the same time, it should be noted that the rather small size of the calculation cell used does not allow us to claim that the observed mechanism of the formation of the tetrahedral Ge sites is the only one operative; other ways of structural relaxation leading to the formation of the tetrahedral sites cannot be excluded

The creation of Ge-Ge bonds in the amorphous phase observed in our simulations, has been suggested previously from EXAFS measurements.[14,22] All studies performed on as-deposited amorphous films consistently found the presence of Ge-Ge bonds. In a similar work performed on a laser-amorphized amorphous phase, i.e., the phase obtained not from the vapor but from a solid crystalline phase, did not reliably detect the Ge-Ge bonds although their inclusion into the fitting procedure did improve the fit quality. The comparison of the experimental XANES data between the as-deposited and laser-amorphized amorphous phases suggests that the number of Ge-Ge bonds, which is likely to correlate with the presence of tetrahedral Ge atoms (cf. Fig. 1, panel 4), is larger—and hence more readily detectable—in the as-deposited phase.[9] The larger concentration of tetrahedral Ge sites in as-deposited samples has also been suggested by *ab initio* simulations.[23]

A question that arises is why, and how, two Ge atoms that are close to each other can form an additional covalent Ge-Ge bond when all valence electrons are already consumed. To address this issue, we built a hypothetical GeTe cubic cluster with four
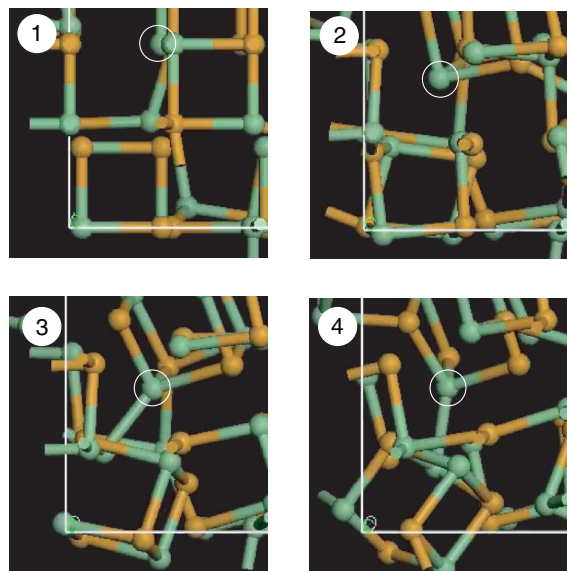

FIG. 1. (Color online) Disordering of GeTe observed by DFT simulations. Frames 1–4 show the formation of tetrahedral Ge sites located at corners of neighboring $ABAB$ cubes. Te atoms are shown in orange and Ge atoms are shown in green. The Ge atom in question is encircled by a white ring. Frame 1: the ititial stage of disordering process; frame 2: $ABAB$ cubes start to misorient; frame 3: an additional Ge-Ge bond is formed while the structure still preserves the cubic shape; frame 4: tetrahedral local geometry is established.

Ge atoms and four Te atoms. Considering the coordination of species and bonding angles it is reasonable to expect pure *p* bonding between the atoms located at the cube corners. The energy diagrams for Ge and Te atoms involved in this kind of bonding are shown in Fig. 3 (left panel). The difference between bonding within this cubic cluster and the cubic crystalline phase of GeTe is twofold. First, the sense of dihedral angles is different, and secondly—and more importantly—the absence of long-range order in the former case.

After the structure has been relaxed, the Ge-Te bonds acquire interatomic distances of 2.77 Å, i.e., shorter than the value characteristic of the bulk crystalline phases (2.83 Å) but very similar to that in pyramidal sites in the covalently bonded amorphous phase[9] that does not possess resonant interaction.

As a means to study the nature of interatomic interaction we first calculated charge density difference (CDD) between the model in question and isolated pseudoatoms. As the name implies, CDD shows redistribution of electrons resulting from interatomic interaction, i.e., chemical bonding. Within the CDD approach, covalent bonds resulting from an overlap of orbitals with two electrons are characterized by an increased charge density midway between the two participating atoms. CDD isosurfaces for the GeTe cube are shown in Fig. 2 (left panel). As expected, a charge pileup, that is a signature of a covalent bond, is observed between any two atoms in the cube.

Unexpectedly, there is also a charge pileup outside the Ge atoms along the cube diagonals. One possibility for its existence would be merging of the three back lobes of the orbitals that participate to form the covalent bonds. It is due to the interaction between the back lobes that the long-range order in the crystalline GeTe is established. Should this be the case, however, one would expect a similar charge pileup next to Te atoms, which is clearly not the case. An alternative explanation is that, despite the almost 90° bonding geometry (the angles subtended by Ge atoms are in fact close to 96°), the Ge atoms are (partially) sp^3 hybridized.

The CDD approach described above is just one of the ways to analyze the electron (charge) distribution. Another popular method to investigate bonding is the electron localization function (ELF), which has been argued to be more sensitive

FIG. 3. (Color online) Atomic and molecular diagrams for Ge and Te atoms in GeTe. Left panel corresponds to pure *p*-type bonding in the ordered phase; right panel corresponds to the formation of sp^3-hybridized Ge orbitals shown in Fig. 2.

to nonbonding electron pairs.[24] We also performed ELF simulations and the result (Fig. 2, right panel) also demonstrates that nonbonding lone-pair orbitals are located at Ge atoms. Considering the bonding geometry, the result confirms that upon the formation of a GeTe cube a pair of nonbonding electrons is transferred from Te atoms to Ge sp^3 orbitals. The energy diagrams for this case are shown in Fig. 3 (right panel). The sp^3 hybridization of Ge orbitals in the amorphous phase has been further confirmed by calculation of the local projected density of states and is also in agreement with similar calculations performed by others.[12]

We have also examined the case of a single covalently bonded GeTe layer that was allowed to relax in plane; the result is shown in Fig. 4. In this case, Ge-Te bond lengths have a very similar value of 2.76 Å and Ge atoms also possess lone-pair electrons on sp^3-hybridized orbitals, which demonstrates that the appearance of lone-pair electrons is not associated with the shape of the cluster but with the absence of resonant bonding associated with long-range order. Finally, the generality of the result has been confirmed using an amorphous structure of GeTe generated in Ref. 21, which also has lone pairs on sp^3-hybridized Ge orbitals (Fig. 5). In the latter case, lone-pair orbitals can also be found on Te atoms.

The above results demonstrate that in stark contrast to the crystalline phase where all valence electrons are used up for bonding, amorphous GeTe *is* a lone-pair semiconductor with an important difference from chalcogenide classes being that the lone-pair electrons in GeTe are localized on Ge atoms,
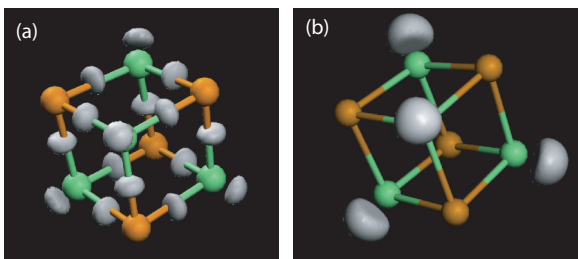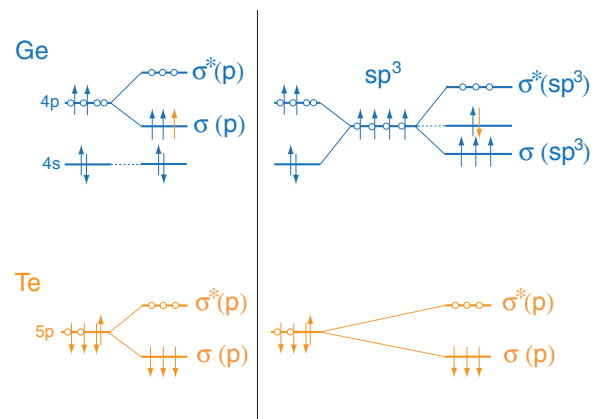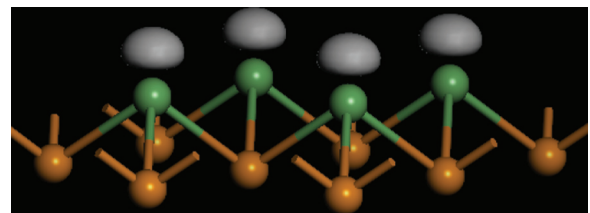

FIG. 2. (Color online) CDD (left) and ELF (right) isosurfaces, shown in gray, for a GeTe cubic cluster obtained from DFT simulations. Ge atoms are green and Te atoms are orange as in Fig. 1. In CDD, Te atoms only exhibit a charge increase midway along the Ge-Te bonds that correspond to purely *p*-orbital bonding. At the same time, Ge atoms additionally possess an increased charge along the cube diagonals that indicates a significant sp^3 hybridization despite nearly normal bonding angles. The ELF isosurfaces also clearly demonstrate that the nonbonding electron pair is transferred from the *p* orbitals of Te atoms to the sp^3 orbitals of Ge atoms.

FIG. 4. (Color online) ELF isosurfaces for a single covalently bonded GeTe layer demonstrating the presence of lone-pair electrons on sp^3-hybridized Ge orbitals.
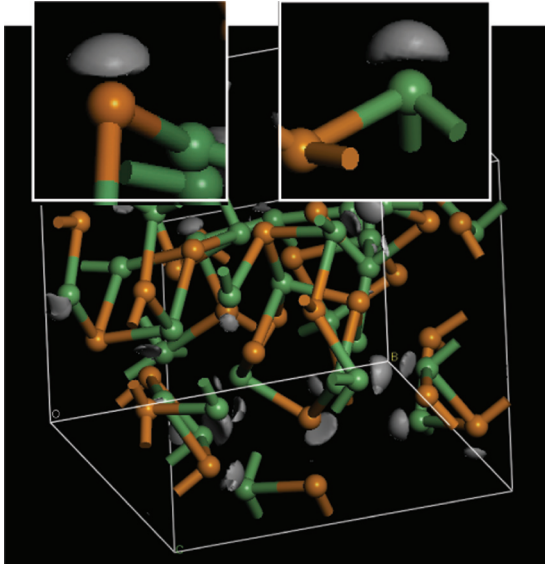
FIG. 5. (Color online) ELF isosurfaces calculated for the relaxed amorphous phase obtained from ideal GeTe demonstrate the presence of nonbonding lone-pair orbitals in the structure. The insets show zoomed-in images of a twofold coordinated Te atom and threefold coordinated Ge atom.

while in chalcogenide glasses they are localized on chalcogen species. At the same time, the presence of a large concentration of doubly occupied nonbonding lone-pair orbitals suggests that all—or most—of the conclusions drawn previously for chalcogenide glasses can also be applied for amorphous GeTe-based phase-change alloys, in particular, the pinning of the Fermi level in the middle of the gap.

As we discussed earlier, the amorphization process consists of the rupture of the longer Ge-Te bonds and subsequent lattice relaxation. When two pyramidally coordinated Ge atoms find themselves close to each other, an additional Ge-Ge bond can be formed transforming pyramidal Ge atoms into tetrahedrally coordinated. The formation of the tetrahedral sites at the expense of the pyramidal sites (Fig. 1, panels 3 and 4) demonstrates that locally sp^3-hybridized atoms are energetically more favorable and is facilitated by the fact that Ge orbitals are already sp^3 hybridized. This process is schematically illustrated in Fig. 6 where two pyramidal sites shown in the upper part of the figure transform into two tetrahedral sites shown in the lower part. The corresponding energy diagrams for the Ge atoms are shown next to the structural fragments.

One can see that when the tetrahedral sites are formed using the two lone-pair orbitals, two additional electrons appear in the antibonding states, i.e., in the conduction band (or its tail). As can be easily seen, the energy difference between the nonbonded and bonded cubic fragments is very small. The energy gain for the formation of the extra bonds comes from the structural relaxation when the sp^3-hybridized Ge orbitals can acquire their preferred tetrahedral bonding angles. It should be noted that a similar mechanism, i.e., the formation of additional interchain (interlayer) bonds through use of lone-pair electrons, has been proposed previously to explain the observed increase in coordination number in the photoexcited
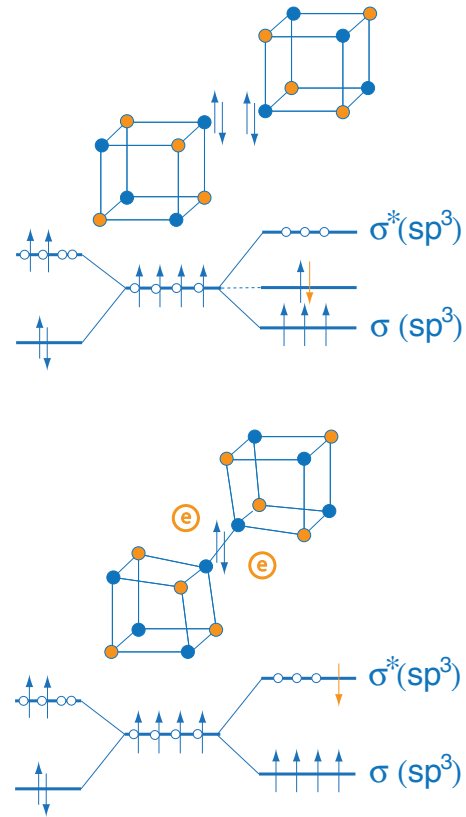

FIG. 6. (Color online) Schematics of the formation of tetrahedral Ge sites forming a Ge-Ge bond. The upper panel corresponds to an initial stage of disordering when cubiclike bonding angles are preserved; the lower panel depicts the final stage. In the upper part of each panel atomic structures are shown and in the lower part the corresponding energy diagram for the Ge atoms. As a result of the formation of tetrahedral Ge sites (and the Ge-Ge bond), additional free electrons are generated.

state of chalcogenide glasses[25] that are well-known lone-pair semiconductors.[3]

The presence of the free electrons in the conduction band and their gradual recombination as the structure relaxes, may be the reason for the conductivity drift observed experimentally, an effect that hinders the wide use of multilevel recording.[15,26] The conductivity drift (decrease) has an extended exponential time dependence. Schematically, the drift phenomenon is illustrated in Fig. 7. After an application of
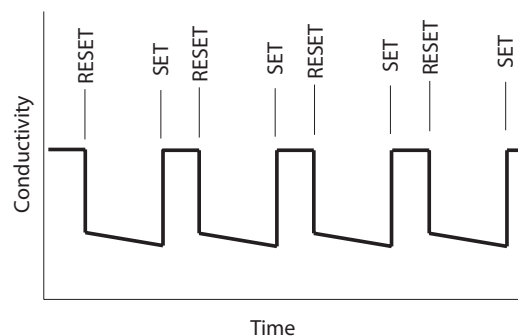

FIG. 7. Schematics of the drift phenomenon. See text for details.

a RESET pulse, the conductivity drops as a result of the amorphization process. Following the initial drop, the conductivity gradually decreases—drifts—which is usually attributed to structural relaxation without any further details discussed. The drift continues until an application of a crystallizing SET pulse. Different trends of the conductivity change during the drift (decrease) and crystallization (increase) do not allow one to directly associate drift with gradual ordering of the structure and suggest that electronic processes may be involved.

Upon the structural relaxation towards the crystalline phase, the Ge-Ge bonds are broken, resulting in destruction of the tetrahedral sites and a partial recombination of free electrons and hence in a decrease in the concentration of free charge carriers with a concomitant decrease in conductivity. The process continues until the establishment of long-range order in the structure when the conductivity abruptly increases due to an increased mobility of charge carriers in the ordered phase. The opposite trends in the conductivity change during the drift and crystallization are thus related to two different processes, viz., a change in the carrier concentration upon destruction of the tetrahedral sites and a change in mobility upon crystallization. Experiments using techniques sensitive to the presence of tetrahedral Ge sites, such as Ge L-edge XANES[27] are required to confirm, or negate, the proposed mechanism. Such measurements are currently under way.

The gradual decrease in conductivity upon recombination of the electrons originating from the Ge-Ge bonds is reminiscent of persistent photoconductivity (when the conductivity remains higher after exposure to light), also described by an extended exponential function and having a characteristic time of days. It may be informative to note that persistent photoconductivity has been observed upon excitation of chalcogenide glasses at low temperature[28] (so that the structural relaxation is inhibited) and attributed to the formation of interchain (interlayer) bonds generated due to photoexcitation with a concomitant generation of electrons.

The formation of the locally stable tetrahedral Ge sites and Ge-Ge bonds is also the likely reason for the stability of the amorphous phase. Indeed, in order to establish long-range order, such bonds must be broken, which ensures a rather high activation barrier of 2.3 eV on the way to crystallization.

In summary, in this work we demonstrated that despite the bonding angles close to $90°$, Ge species in GeTe without long-range order are sp^3 hybridized and possess nonbonding lone-pair electrons, i.e., amorphous GeTe is a lone-pair semiconductor similar to chalcogenide glasses with the difference that in the latter lone-pair electrons are localized at chalcogen species. As a result, structural defects existing in chalcogenide glasses, valence alternation pairs in particular, may also exist in amorphous GeTe and determine its electronic properties such as the pinning of the Fermi level in the middle of the gap. The formation of additional Ge-Ge bonds between two pyramidal sites that generates tetrahedral configurations provides a natural explanation for the high stability of the amorphous phase; their gradual dissociation as the structure relaxes below the crystallization temperature is a likely microscopic reason for the conductivity drift in the amorphous phase.

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