Physics of Semiconductors.
Computer materials science

UDC 538.9

EDN YXMPGU
https://www.doi.org/10.33910/2687-153X-2026-7-1-16-21

The formation of dimers in the gaseous phase of GeTe as a way to fabricate vacancy-free crystalline thin films

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For citation: Kolobov, A. V. (2026) The formation of dimers in the gaseous phase of GeTe as a way to fabricate vacancy-free crystalline thin films. *Physics of Complex Systems*, 7 (1), 16–21. https://www.doi.org/10.33910/2687-153X-2026-7-1-16-21
EDN YXMPGU

Received 18 December 2025; reviewed 16 January 2026; accepted 16 January 2026.

Funding: The research was supported by an internal grant of Herzen State Pedagogical University of Russia (project No. 43-ВГ).

Abstract. Germanium telluride (GeTe) is a multifunctional material with a plethora of useful properties. In particular, it is one of the best thermoelectric materials. Its thermoelectric properties are affected by intrinsic Ge vacancies that are always present in the crystalline phase because of the low formation energy of such defects. This work draws on ab initio molecular dynamics simulations, demonstrating that due to a very special nature of bonding, often called 'resonant' and/or 'metavalent', the materials evaporate as GeTe dimers rather than individual molecules. We argue that this feature can be used to fabricate oriented vacancy-free GeTe films when the material is thermally evaporated onto a heated templating substrate.

Keywords: phase-change materials, germanium telluride, ab initio molecular dynamics, resonant bonding, evaporation, dimers

Introduction

GeTe is a multifunctional material which is (i) a semiconductor (Li et al. 2025), (ii) a superconductor at high pressure (Cheng et al. 2024), (iii) a ferroelectric (Kolobov et al. 2014), (iv) a material with a giant Rashba effect (Liebmann 2016), (v) one of the best thermoelectric materials (Perumal 2016) and (vi) a prototypical phase-change material (Singh 2023). Obviously, such a plethora of useful properties is determined by its structure. In this work, we demonstrate that despite its three-dimensional structure, strong covalent bonding exists between *pairs of atoms* that form Ge-Te *dimers*. The interaction between the dimers is much weaker, yet it is this weaker interaction that determines the integrity of its crystal structure (Kolobov et al. 2011). This work shows that GeTe consequentially evaporates as dimers rather than individual molecules. We suggest that the dimerised gaseous phase of GeTe may pave the way for fabricating vacancy-free GeTe films.

In order to understand the function, one has to study the structure (Jones 2025). What is therefore unusual about the structure GeTe? The first question is how a cubic structure can be formed when Ge tends to be sp3-hybridised and tetrahedrally coordinated. The reason for the unusual geometry

of bonds in GeTe lies in the mutual electronic configurations of Ge and Te. Germanium is a group 14 element and as such has 2 electrons located on 3 p-orbitals. Consequently, one p-orbital is empty. Tellurium, on the other hand, has 4 electrons on 3 p-orbitals, so that one orbital has two electrons called a 'lone-pair'. This electronic configuration allows for the formation of a cubic structure where one covalent bond is formed using the Te lone-pair electrons as shown in Fig. 1.

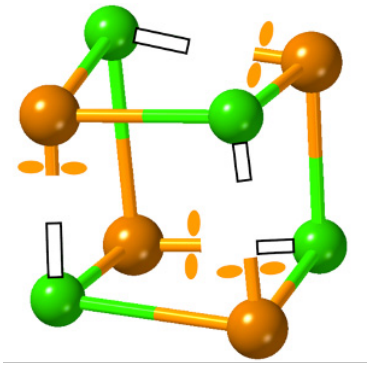

Fig. 1. Formation of a cubic GeTe building block

It is clear that all covalent electrons are consumed in the shown structure. The next question is therefore how a three-dimensional rock-salt structure of GeTe can be formed from these cubes (Fig. 2a). To answer this question, Fig. 2b presents the formation of a covalent bond using two p-orbitals. When the wave functions on the two atoms (shown as '+' and '–' signs in the Figure) have the same symmetry, a covalent bond is formed. On the other hand, when the symmetry is opposite, an antibonding state is formed. One can thus imagine that covalent bonds develop between pairs of Ge and Te atoms with the '+' symmetry of the wave functions along the …Ge–Te–Ge–Te–Ge–Te… atomic sequence in the rock-salt-like structure as shown in Fig. 2c. A careful examination of this linear structure reveals that the symmetry of the wave functions *between* the covalently bonded *pairs* is also the same ('–' as shown in Fig. 2c, above). The same symmetry of the wave functions associated with the back-lobes of the p-orbitals used for bonding suggests that bonding could have taken place between alternative pairs of atoms with the '–' symmetry of the wave functions as shown in Fig. 2c (below).

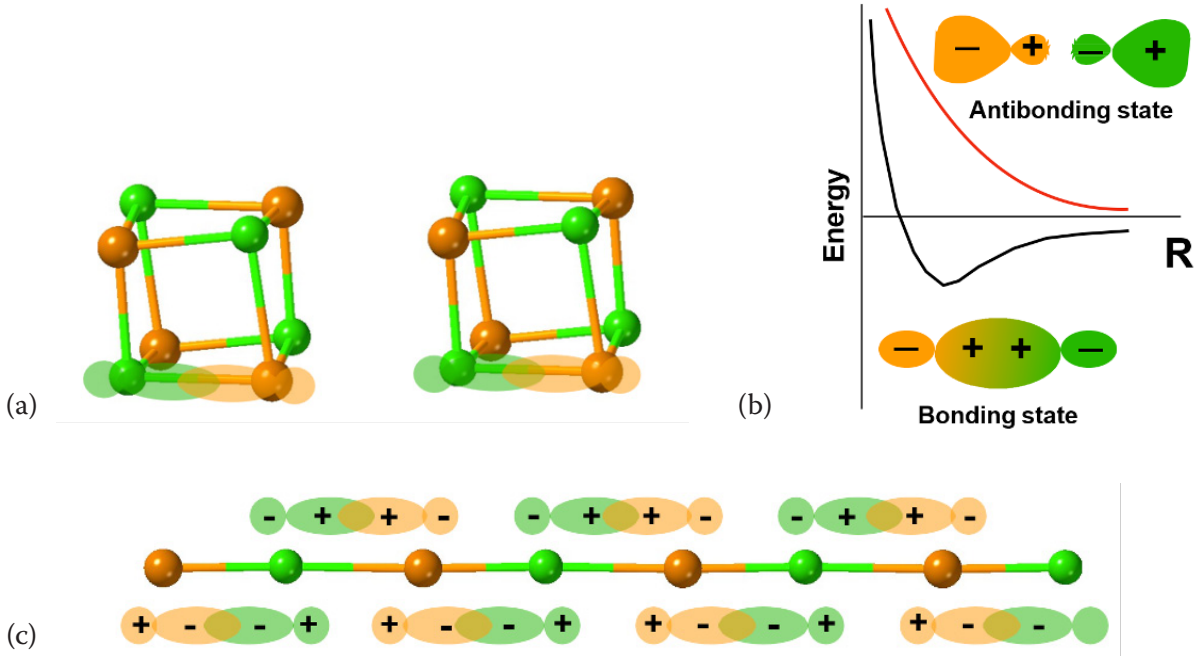

Fig. 2. (a) Individual Ge_4Te_4 cubes with all saturated covalent bonds. (b) Interaction of p-orbitals with the same symmetry (+ and +) leads to the formation of a bonding state, while the orbitals with the opposite symmetry (+ and –) give rise to an antibonding state. (c) Two possible bonding configurations in a linear chain of Ge/Te atoms result in the formation of a resonant/metavalent bond

Since the two structures have the same energy, a resonance between them is possible, and this kind of bonding in GeTe was called 'resonant' in the pioneering paper (Lucovsky, White 1973). Subsequently, the approach was developed in (Shportko 2008), and eventually the term 'metavalent bonding' was suggested (Wuttig 2018). We shall use these terms below, although the concept of metavalency has recently been debated (Jones et al. 2023). Since p-orbitals are orthogonal, the overlap between them is minimal, and the three directions can be considered independently. Within this framework, the structure is a one-dimensional linear chain of alternating Ge and Te atoms. As such, it is subject to the Peierls distortion, which results in the formation of alternating shorter and longer bonds in three directions. In other words, the structure can be viewed as Ge-Te dimers connected by weaker bonds through the back-lobe interaction. It may be interesting to note here that due to the p-orbital bonding Se confined in channels of cancrinite also formed dimers (Kolobov et al. 1999).

(Bragg) neutron diffraction measurements suggested that upon heating to 720 K, the rhombohedral distorted structure with shorter and longer bonds changes to the rock-salt cubic phase with all equal Ge-Te bonds (Chattopadhyay, Boucherle 1987). It should be kept in mind, however, that Bragg diffraction measures the average structure that is not sensitive to local distortions (Stern 1996). Techniques that are sensitive to local distortions, such as extended X-ray absorption fine structure (EXAFS) or pair-distribution function (PDF) analysis of diffraction patterns, unambiguously demonstrated that, in fact, the shorter and longer bonds persist through the ferroelectric-paraelectric transition (Fons et al. 2010; Matsunaga et al. 2011). The presence of the shorter and longer bonds was further found in liquid GeTe, which was named 're-entrant Peierls distortion' (Raty 2000). We note here that this term is apparently incorrect, since, as just mentioned above, the shorter and longer bonds never disappeared in the first place. Since the bonding hierarchy between the shorter and longer bonds persists from low temperature to molten phase, it is thus natural to expect that GeTe will evaporate as Ge-Te dimers when the weaker shorter bonds break, while the stronger shorter bonds will be preserved. This hypothesis was verified in this work by ab initio molecular dynamics (AIMD) simulations.

AIMD simulations were performed using density functional theory (DFT) within the generalized gradient approximation (GGA) with the PBE exchange-correlation functional (Perdew 1996) and the plane wave basis set as implemented in the pseudopotential-based CASTEP code (Clark et al. 2005; Segall 2002). To describe the electron-ionic interactions, Vanderbilt ultrasoft pseudopotentials (Vanderbilt 1990) and cut-off energy $E_{cut\text{-}off}$ = 230 eV were chosen. The starting structure was a GeTe cube with the Te–Ge–Te–Ge atomic sequence (i. e. two connected dimers) along each edge placed in a simulation box with the 30 × 30 × 30 nm size (Fig. 3a). Taking into account the relatively large size of the supercell and consequently the small volume of the Brillouin zone (BZ) used for AIMD simulations, only G-point was used when integrating over the BZ. The GeTe cube was heated to 4,000 K, i. e. well above the melting point (T_m ~ 1,000 K) and held at this temperature for 15 ps. The simulations were carried out using the NVT ensemble with a Langevin thermostat (to maintain ergodicity) with a time step of 4 fs.

As the system was heated and kept at the high temperature, the crystal structure melted, and the evaporation process started. Fig. 3 shows several frames of this process. Note that the simulation box is not shown in the figure. One can see that what is evaporated are not individual molecules but Ge-Te dimers, which confirms the idea that the structure is formed by weakly interconnected dimers.

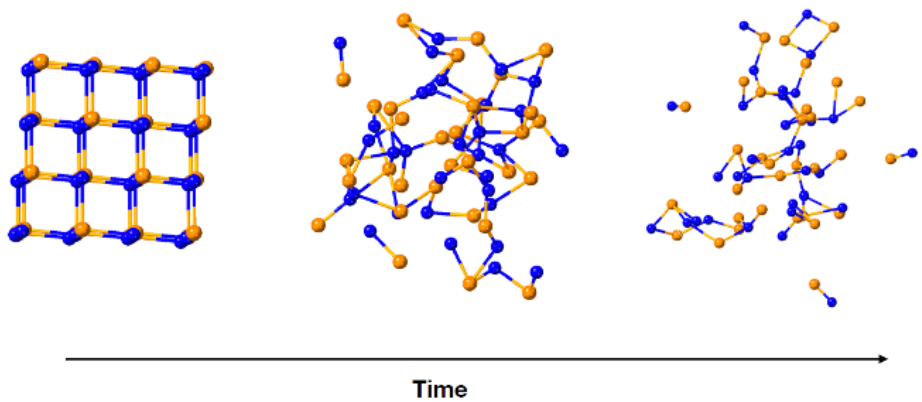

Fig. 3. Ab initio molecular dynamics simulations of the evaporation of GeTe

 https://www.doi.org/10.33910/2687-153X-2026-7-1-16-21

This finding has an important consequence and suggests a way to fabricate vacancy-free GeTe. This is an important technological problem, since bulk GeTe crystals and crystallised GeTe films always contain 5–10% vacancies on Ge sites. Below we propose a way to fabricate vacancy-free GeTe. Indeed, RF sputtering that is usually used for thin film fabrication is a rather energetic process breaking all bonds in the target materials and is likely to generate a flux of individual Ge and Te ions randomly arriving at the substrate and forming a random amorphous chemically disordered network. At the same time, thermal evaporation at elevated temperatures is likely to produce a chemically ordered phase. This is illustrated in Figs. 4 and 5.

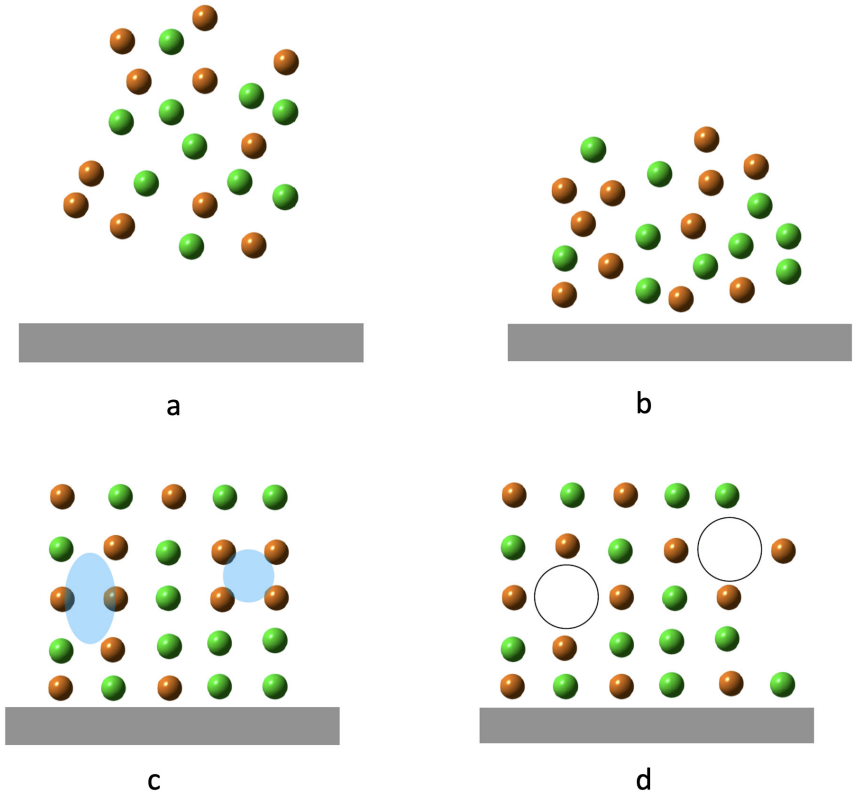

Fig. 4. Vacancy formation upon crystallisation from an amorphous phase. (a) Ge and Te atoms deposition, (b) amorphous phase, (c) chemically disordered crystalline phase. Increased electron density in Te-rich regions (shown in light blue) leads to repulsion between Te atoms leading to the formation of a structure with vacancies

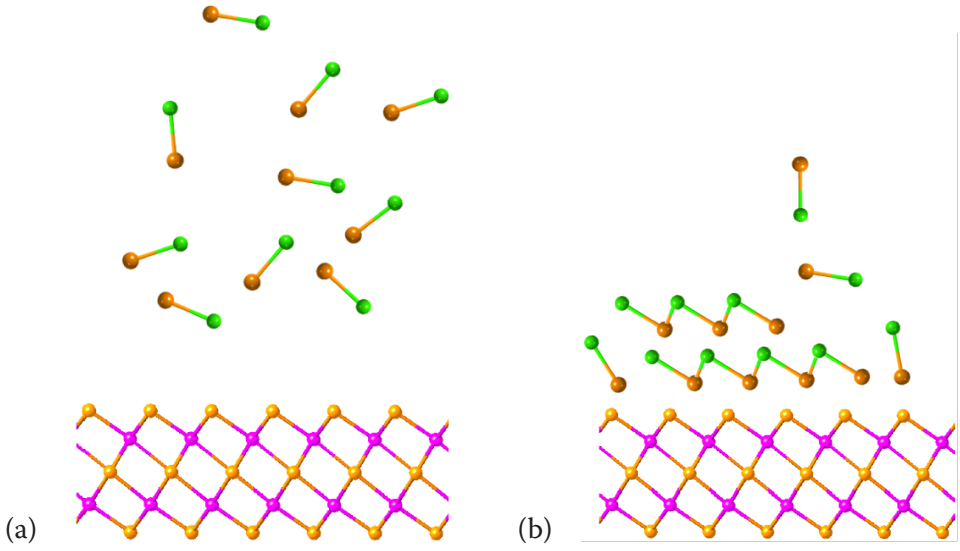

Fig. 5. Formation of vacancy-free GeTe from Ge-Te dimers on a heated templating substrate. (a) Dimers in the vapour phase. (b) Dimers get ordered by the substrate forming vacancy-free GeTe

In the case of RF sputtering, upon crystallisation, there may be Ge-rich and Te-rich microregions as shown in Fig. 4. Since Te atoms possess non-bonding lone-pair electrons, they will repel each other, leading to the formation of vacancies. The presence of vacancies in GeTe films obtained through solid state crystallisation has been demonstrated using EXAFS (Kolobov et al. 2003), and the low formation energy of this process was argued to be the origin of p-type conductivity of GeTe (Edwards et al. 2005).

On the other hand, if a film is obtained by thermal evaporation onto a heated substrate acting as a template, such as Sb_2Te_3 (Simpson 2012), one can expect that dimers, at certain temperature regimes, will arrange themselves into a vacancy-free phase (Fig. 5). Experiments to verify this idea are currently underway. If successful, they may pave the way for creating GeTe with desired vacancy concentration, which may be very beneficial for the fabrication of GeTe-based thermoelectric devices, where the presence and distribution of vacancies play an important role (Zhang 2018).

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

Acknowledgements

I am grateful to my students for preparing input files for the simulations.

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