CHIN. PHYS. LETT. Vol. 38, No. 2 (2021) 026103

First-Principles Study of Intrinsic Point Defects of Monolayer GeS

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(Received 13 November 2020; accepted 18 December 2020; published online 27 January 2021)

The properties of six kinds of intrinsic point defects in monolayer GeS are systematically investigated using the "transfer to real state" model, based on density functional theory. We find that Ge vacancy is the dominant intrinsic acceptor defect, due to its shallow acceptor transition energy level and lowest formation energy, which is primarily responsible for the intrinsic p-type conductivity of monolayer GeS, and effectively explains the native p-type conductivity of GeS observed in experiment. The shallow acceptor transition level derives from the local structural distortion induced by Coulomb repulsion between the charged vacancy center and its surrounding anions. Furthermore, with respect to growth conditions, Ge vacancies will be compensated by fewer n-type intrinsic defects under Ge-poor growth conditions. Our results have established the physical origin of the intrinsic p-type conductivity in monolayer GeS, as well as expanding the understanding of defect properties in low-dimensional semiconductor materials.

DOI: 10.1088/0256-307X/38/2/026103

In the past decade, two-dimensional (2D) materials have attracted considerable attention due to their intriguing physical properties such as high carrier mobility, large on/off ratios, and suitable bandgap.[1–7] Monolayer (ML) GeS is a typical group Ⅳ–Ⅵ compound semiconductor, the structure of which is similar to that of black phosphorene.[8] ML GeS is considered to be a promising alternative for use in novel microelectronic and optoelectronic devices,[9–11] by virtue of its high absorption coefficient ($\sim 10^5\,\mathrm{cm}^{-1}$),[10,12] proper bandgap,[13,14] and high thermoelectric figures of merit (ZT).[15,16] As the technological application of semiconductors depends crucially on the dopability of materials,[17,18] a comprehensive understanding of the intrinsic defects in ML GeS is exceedingly important for applications of ML GeS in novel electronic and optoelectronic devices.

Lately, both bulk SnS[19] and SnSe,[20] two group Ⅳ–Ⅵ compounds which could be described as "cousins" of GeS, have been demonstrated to be native p-type semiconductors. Theoretical research based on first-principles study indicates that their intrinsic p-type conductivity originates from cation vacancies.[21,22] Recent experiments have found that GeS is also an inherent p-type semiconductor.[11,23,24] For example, Tan *et al.* have succeeded in fabricating field-effect transistors (FETs) based on thin flakes of multilayer GeS; they observed a typical p-type behavior in which the current increases with increasing V_{ds}.[11] These results indicate the presence of existing shallow acceptors in ML GeS. However, there has to date been no comprehensive investigation of the physical origin of p-type conductivity in ML GeS, an omission which could seriously restrict its application and development in practical devices.

As is well known, for defects in 2D semiconductors, the traditional standard approach, the so-called Jellium model, contains a computational difficulty, in which the formation energy of charged defects will diverge as the vacuum region increases, due to the unrealistic charge distribution in vacuum region.[25,26] Recently, a more reasonable approach, known as the "transfer to real state" model (TRSM) has been proposed, to accurately calculate the formation energies and transition levels of charged defects.[26] This model avoids the divergence caused by the artificial long-distance electrostatic energy encountered by the Jellium model. We therefore adopt this model to pro-

Supported by the National Natural Science Foundation of China (Grant Nos. 61922077, 11804333, 11704114, 11874347, 61121491, 61427901, 11634003, and U1930402), the National Key Research and Development Program of China (Grant Nos. 2016YFB0700700 and 2018YFB2200100), the Science Challenge Project (Grant No. TZ2016003), and the Youth Innovation Promotion Association of Chinese Academy of Sciences (Grant No. 2017154).

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vide reliable data regarding the formation energies and transition levels of charged defects.

In this Letter, we systematically investigate the formation energies and transition energy levels of all intrinsic point defects in ML GeS based on the TRSM. Our calculations indicate that (i) the inherent p-type conductivity in ML GeS under equilibrium growth condition arises from intrinsic germanium vacancy (V_{Ge}) defects; (ii) the three nearest S atoms around V_{Ge} move away from the vacancy site after atomic relaxation, which introduces a shallow transition level in ML GeS. Our results, therefore, pinpoint the physical origin of the intrinsic p-type conductivity in ML GeS, as well as expanding our understanding of defect properties in low-dimensional semiconductor materials.

Computational Method and Formulation. The first-principles calculations were performed using the plane-wave pseudopotential approach, implemented using the quantum expresso (QE) package.[27,28] The Perdew–Burke–Ernzerhof approximation[29] was adopted to simulate exchange-correlation interactions. The kinetic cutoff energy for the plane-wave basis sets was 60 Ry. All atoms were relaxed until the Hellman–Feynman forces on individual atoms fell below 10^{-8} Ry/Bohr.

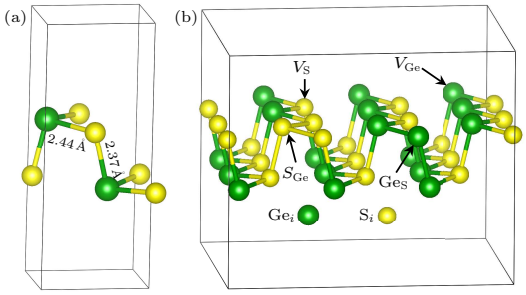

Fig. 1. Schematic plot of (a) optimized atomic structure of monolayer GeS in a unit cell with two different bond lengths showing, (b) local structure of a monolayer GeS with all kinds of intrinsic point defects. The green and yellow balls represent Ge and S atoms, respectively.

As shown in Fig. 1(a), the optimized lattice constants of monolayer GeS are $a = 4.31$ Å, $b = 3.61$ Å, which agree well with previous reports.[14,30] The corresponding bond lengths of Ge–S were calculated to be 2.44 Å and 2.37 Å for axial and planer bonds, respectively. To avoid the interaction of defects between the periodic supercells, a $6 \times 6 \times 1$ (144 atoms) monolayer supercell with a vacuum zone of 20 Å was selected to study the fundamental properties of native defects in ML GeS. Intrinsic defects were introduced by removing one Ge/S atom (V_{Ge}/V_S), attaching one Ge/S atom on the crystal surface (Ge_i/S_i), and substituting one Ge/S atom with an antisite atom (Ge_S/S_{Ge}), as shown in Fig. 1(b). All of the intrinsic defects mentioned in this study are confirmed to be the most stable varieties. The distance between adjacent point defects is more than 20 Å in three dimensions, providing reasonable results with respect to the formation energies and transition energy levels of native defects.

The formation energy (ΔH_f) of a supercell containing a defect α in charge state q is defined by[26]

$$\Delta H_f(q,\alpha) = E_{tot}(q_{\varepsilon_D \to \varepsilon^h_{C,V}}, \alpha) - E_{tot}(\text{host}) + \sum_i n_i(E_i + \mu_i) + q\left(\varepsilon_F - \varepsilon^h_{C,V}\right), \quad (1)$$

where $E_{tot}(q_{\varepsilon_D \to \varepsilon^h_{C,V}}, \alpha)$ is the total energy of the supercell containing a defect α in charge state q; $E_{tot}(\text{host})$ is the total energy of the host supercell; n_i is the number of elements transferred from the host supercell to reservoirs in forming defects; μ_i is the chemical potential of atom i with respect to energy $E(i)$ for the stable solid/gas; q is the number of electrons transferred from defect level to valence band maximum (acceptor, $q < 0$) or conduction band minimum (donor, $q > 0$). The eigenvalues between different cells should be aligned at the same reference level.[26]

Equation (1) indicates that the formation energy of defects are reliant on the selected chemical potentials.[31] Therefore, under thermodynamic equilibrium conditions, the growth of ML GeS crystal requires that

$$\mu_{GeS} = \mu_{Ge} + \mu_S, \quad (2)$$

where μ_{GeS} is the chemical potential of monolayer GeS. If we set $\mu_i = 0$ for their stable solid/gas phases, then the calculated formation enthalpy of monolayer GeS will be $\mu_{GeS} = -0.5$ eV. In addition, the chemical potentials are limited so as to prevent the formation of elemental substances by means of the following expressions:

$$\mu_{Ge} \leqslant \mu(\text{Ge}) = 0, \quad (3)$$

$$\mu_S \leqslant \mu(\text{S}) = 0. \quad (4)$$

We are therefore able to confirm two extreme conditions: Ge-rich (S-poor), and S-rich (Ge-poor), in which the chemical potentials are $\mu_{Ge} = 0$ eV, $\mu_S = -0.5$ eV and $\mu_{Ge} = -0.5$ eV, $\mu_S = 0$ eV, respectively. Finally, to avoid phase separation into GeS_2, we also calculated the formation enthalpy of GeS_2, confirming that a GeS_2 phase will not form in the range of chemical potentials for the formation of the GeS phase.

The transition energy level of a defect α between charge states q and q', denoted by $\varepsilon_\alpha(q/q')$ is defined as[31]

$$\varepsilon_\alpha(q/q') = \frac{[E_{tot}(q_{\varepsilon_D \to \varepsilon^h_{C,V}}, \alpha) - E_{tot}(q'_{\varepsilon_D \to \varepsilon^h_{C,V}}, \alpha)]}{(q' - q)} + \varepsilon^h_{C,V}. \quad (5)$$

It should be noted that, besides the neutral states, all intrinsic defects arising in this work are charged in this range from $q = -2$ to $+2$.

Results and Discussion—Electronic Properties of Monolayer GeS. Before studying the properties of the intrinsic defects in ML GeS, we first analyze the electronic structure, as well as the partial density of states (PDOS), of natural ML GeS. As shown in Fig. 2(a), ML GeS has an indirect bandgap of 1.66 eV, which is consistent with previous reports.[30,32,33] The valence band maximum (VBM) is situated on the Γ–X path, while the conduction band minimum (CBM) locates on the Y–Γ path. Based on the PDOS in Fig. 2(b), we find that the upper states of the valence band of ML GeS consist primarily of the S 3p orbitals, and partially of Ge 4p and Ge 4s orbitals, whereas the Ge 4s states make only a slight contribution to the lower states of the valence band. This indicates that lower-energy valence band states in the range from −7.0 to −5.0 eV may be ascribed to the interaction between S 3p and Ge 4p states, whereas the upper states of the valence band from −4.0 to −3.0 eV are derived from the interaction between Ge 4p, Ge 4s, and S 3p orbitals, resulting in the formation of anti-bonding states. Moreover, the conduction band states are principally composed of Ge 4p and S 3p states, while Ge 4s states contribute slightly to the conduction band. For a more in-depth understanding, we further plotted the partial charge densities of the VBM and CBM states of ML GeS in Figs. 2(c) and 2(d), respectively. The charge distributions are clearly consistent with the PDOS, in which the VBM states depend primarily on the S atoms, and partially on the Ge atoms, whereas the CBM charge evidently prefers to locate around the Ge atoms.

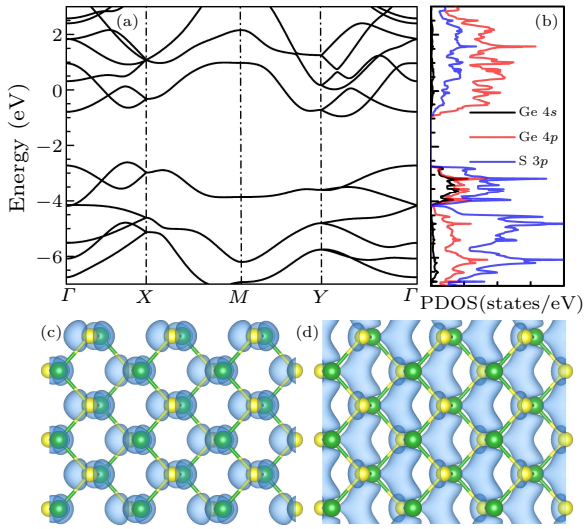

Fig. 2. (a) Band structure and (b) partial density of states (PDOS) of pure ML GeS, respectively. Local structures and three-dimensional partial charge density (blue: isosurface of 0.0001e^-/Bohr^3) for (c) VBM state and (d) CBM state in a GeS supercell. The green-colored balls represent Ge atoms, and the yellow balls denote S atoms.

Formation Energies and Transition Levels of the Intrinsic Defects. Figures 3(a) and 3(b) display the calculated formation energies of intrinsic defects in ML GeS as functions of the Fermi level under Ge-rich (S-poor) and S-rich (Ge-poor) conditions, respectively. The Fermi level ranges from the VBM to CBM, i.e., from 0 to 1.66 eV with respect to host ML GeS. In addition, the charged states of all intrinsic defects are calculated from $q = -2$ to +2, given that the nominal valences of Ge and S atoms in host GeS are Ge^{2+} and S^{2-}, respectively.

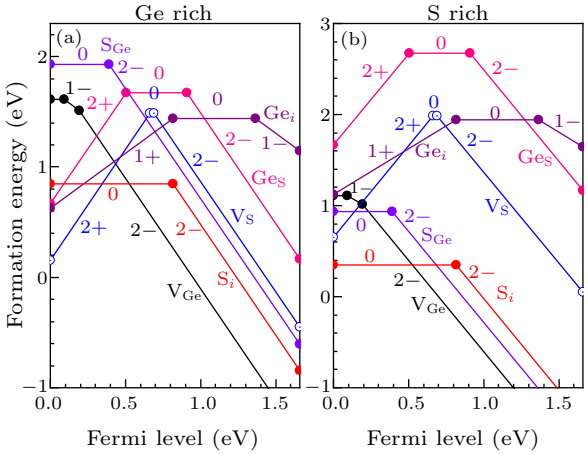

Fig. 3. Calculated formation energies of native defects as a function of Fermi level under (a) Ge-rich, and (b) S-rich limits in ML GeS.

As shown in Fig. 3, the germanium vacancy V_{Ge}, under both growth conditions, has the lowest formation energy of all of the native defects, in which the shallow acceptor defect transition energy level $\varepsilon(0/-)$ is approximately 0.09 eV above the VBM (see Table 2). Therefore, V_{Ge} can act as a shallow acceptor and primary contributor to the intrinsic p-type conductivity of ML GeS. In contrast to V_{Ge}, although V_S has a lower formation energy near the VBM, its ultra-deep defect transition level ε (0/2+) makes it a recombination center rather than an effective donor defect. Therefore, when the hole densities increase constantly with the ionization of V_{Ge}, E_F moves towards VBM and is then pinned at the intersection between V_{Ge} ($q = -1$) and V_S ($q = +2$) under both Ge-rich and S-rich growth conditions, leading to a p-type conductivity in intrinsic ML GeS. As shown in Eq. (1), the formation energy of a defect depends on the atomic chemical potentials; the compensation of V_S to V_{Ge} can therefore be limited under S-rich growth conditions. Furthermore, n-type doping is more difficult than p-type doping in ML GeS, due to the strong natural compensation of V_{Ge}.

In the case of interstitial defects in ML GeS, as compared with the interstitial defects at high formation energies in bulk SnS and SnSe,[21,22] germanium interstitial (Ge_i) has a relative low formation energy (< 2 eV), and sulfur interstitial (S_i) has a lower formation energy (<1 eV), as given in Table 1. This is be-

cause interstitial defects always induce large strain in bulk materials, whereas in ML GeS, interstitial atoms adhere to the lattice surface (see Fig. 1), inducing only a small degree of strain and atomic displacement. As for the lower formation energy of S_i as compared to that of Ge_i under Ge rich conditions, this is because the atomic radius of S atom is much smaller than that of Ge atom, resulting in a smaller strain on the lattice surface when introducing an S atom. Despite all of this, both interstitial defects make almost no contribution to either the n-type or p-type conductivity of ML GeS, since Ge_i is a deep donor, and S_i is a deep acceptor.

Table 1. Formation energies (in units of eV) of intrinsic point defects in ML GeS under a Ge-rich limit ($\mu_{Ge} = 0$) and an S-rich limit ($\mu_S = 0$). The donor (positively charged state) formation energies are given with respect to the CBM ($E_F = 1.66$ eV), while the acceptor (negatively charged state) formation energies are given with respect to the VBM ($E_F = 0$ eV).

Defect	q	Ge-rich	S-rich
V_{Ge}	0	1.11	1.61
	−1	1.20	1.70
	−2	1.40	1.90
V_S	+2	3.98	3.48
	0	1.99	1.49
	−2	3.37	2.87
Ge_S	+2	4.98	3.98
	0	2.67	1.67
	−2	4.49	3.49
S_{Ge}	0	0.93	1.93
	−2	1.72	2.72
Ge_i	+1	1.12	0.62
	0	1.94	1.44
	−1	3.30	2.80
S_i	0	0.35	0.85
	−2	1.98	2.48

Table 2. Transition levels (in units of eV) referenced to VBM for native defects in ML GeS.

Defect	q/q'	$\varepsilon_\alpha(q/q')$
V_{Ge}	0/1−	0.09
	1−/2−	0.19
V_S	2+/0	0.66
	0/2−	0.69
Ge_S	2+/0	0.50
	0/2−	0.91
S_{Ge}	0/2−	0.39
Ge_i	1+/0	0.82
	0/1−	1.36
S_i	0/2−	0.81

In terms of antisite defects, Ge_S has large formation energy under both growth conditions, indicating that only a small amount of Ge_S can form under equilibrium growth conditions. Moreover, the transition level $\varepsilon(2+/0)$ of Ge_S is significantly deep, and can act as a deep donor, so Ge_S exhibits weak compensation in relation to native p-type conductivity. S_{Ge} has lower formation energy under both growth conditions, resulting in a high defect density. Nevertheless, the calculated transition energy level, $\varepsilon(0/-2)$, of S_{Ge} is approximately 0.39 eV above the VBM, signifying that S_{Ge} is a relatively deep acceptor. As a result, S_{Ge} makes almost no contribution to p-type conductivity in ML GeS, because S_{Ge} prefers a neutral state to a charged state when the Fermi level is below 0.39 eV.

Table 3. Ge–S bond lengths (in Å) around defect site in unrelaxed and fully relaxed systems.

	Bond lengths	
Unrelaxed structure	2.37	2.44
Fully relaxed structure	2.31	2.31, 2.35

Electronic and Structural Properties of Germanium Vacancy. Given the discussion above, it is evident that V_{Ge} is the primary source for p-type conductivity in ML GeS. However, there is as yet no deep understanding of the physical origin of the shallow acceptor transition level of V_{Ge}. Therefore, as shown in Fig. 4, we calculated single-particle levels of V_{Ge} in both unrelaxed and fully-relaxed structures[34] and in neutral and charged states, respectively. In general, when a low-valence atom (Ge_S) or a vacancy (V_{Ge} or V_S) substitutes a high-valence atom, the defect states are derived from host valence band states with energy moving upward.[17] The formation of Ge vacancy creates three dangling bonds, containing four S $3p$ electrons in total. The host ML GeS has a point symmetry of C_{2v}, leading to the S $3p$ states splitting into three singlets, the lower two of which are fully occupied, while the highest is unoccupied. Depending on the potential, the two fully occupied states fall into the valence band, and the unoccupied state is above the VBM, therefore V_{Ge} is an acceptor.

Based on Fig. 4, with a variation in defect charge (e.g., from $q = 0$ to -2), the single-particle level of V_{Ge} in an unrelaxed structure rises upward. This can be attributed to the enhancement of Coulomb repulsion between defect and VBM states. After relaxation, the single-particle level of the charged defect (V_{Ge}^{1-} and V_{Ge}^{2-}) is observed to decline in the band gap. We find that for V_{Ge}^{1-} and V_{Ge}^{2-}, the three S atoms nearest to the V_{Ge} move away from the vacancy site due to Coulomb repulsive interaction, leading to a structural relaxation. Thus the remaining S atoms near V_{Ge} have slightly shorter Ge–S bond lengths than those in the unrelaxed structure (see Table 3). In other words, the electrons trapped by S atoms have a lower energy, due to the shorter distance from Ge cations. This energy gain gives rise to a lower single-particle energy level, resulting in a low-energy consumption of electron ionization, i.e., a shallow acceptor transition level in V_{Ge}. These results show that the shallow transition level of V_{Ge} arises from the decrease in strain effect caused by atomic relaxation.

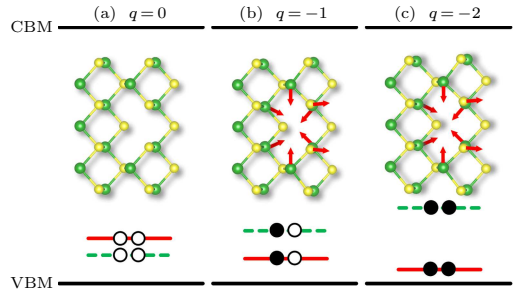

Fig. 4. Calculated single-particle levels of (a) V_{Ge}^{0}, (b) V_{Ge}^{1-}, and (c) V_{Ge}^{2-} in an unrelaxed structure (green dotted line) and a fully relaxed structure (red solid line). All of these levels are referenced to the VBM of the host structure. The black solid and hollow balls indicate the electron-occupied and unoccupied states. The inset figures are plotted to show the local structures containing point defects for (a) an unrelaxed structure and (b), (c) a fully-relaxed structure. The green and yellow balls represent Ge and S atoms, respectively. The red arrows imply the directions of the atomic movements near V_{Ge}.

Exactly as mentioned above, shallow n-type native defects cannot be an efficient source of intrinsic n-type conductivity under either type of equilibrium growth condition. However, p-type conductivity can be readily obtained by virtue of the shallow acceptor V_{Ge} in ML GeS, indicating that ML GeS is a natural p-type semiconductor. This result is in good agreement with previous experimental reports. Furthermore, this conclusion may also expand our understanding of defect properties in low-dimensional materials.

In summary, we have systemically investigated the properties of all kinds of intrinsic point defects in ML GeS, using the TRSM, and based on density functional theory. Our calculations indicate that Ge vacancy can act as a shallow acceptor due to shallow transition level and lower formation energy, which is consistent with the experimental results, indicating the physical origin of p-type conductivity in ML GeS. The local lattice distortion caused by Coulomb repulsion between anions is responsible for these shallow acceptor transition energy levels. On the other hand, n-type doping is much more difficult than p-type doping in ML GeS, due to the intrinsic compensation from V_{Ge}. Our results provide an exhaustive and profound insight into the origin of intrinsic p-type conductivity in ML GeS, as well as furthering our understanding of defect properties in low-dimensional semiconductor materials.

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