An accurate and compact tight-binding model for GeS

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Abstract. In this work we calculate the bands structure for the GeS monolayer from a multi-orbital tight-binding model, where the effect of s-p mixing are considered in slater-Koster equations. The model parameters are adjusting and optimising compared with the band structure obtained by density-functional theory calculation based on the hybrid HSE06 functional. It reproduces the conduction and valence bands as well as the orbital compositions. The anisotropic effective masses and Fermi velocities are identified directly from the anisotropy bands structure.

1. Introduction
A large number of Two-dimensional (2D) materials, as such as graphene, phosphorene, monolayer boron nitride (BN), transition-metal dichalcogenides (TMDs), as well as many others, have been extensively investigated recently [1–3]. Due to their high charge mobility, strong gating capabilities, structural, mechanical, electronic and optical properties, they are expected to be use in electronic, spintronic, and optoelectronic devices [3,4], as a potential substitute for silicon.

The focus now has shifted to the 2D material family is group-VI monochalcogenides (GeSn; GeS, GeSe, GeTe). Among these, GeS is particularly attractive. GeS has high charge mobility, a band gap with a wide range in the visible spectrum, a strong in-plane anisotropy and recently has been experimentally obtain [5,6] by mechanically exfoliated from bulk GeS phase [7–9].

Here, we present an accurate electronic band structure to describe the electronic properties of GeS monolayer, which includes the anisotropy and the effect of s-p orbitals mixing. The electronic band structure was calculated based on an effective multi-orbital tight-binding model. The tight-binding parameters were obtained by a self-consistent and systematic optimization procedure [10], where an orthogonal basis composed of all 3s and 3p orbitals of GeS monolayer was used. The multi-orbital tight-binding model represent the counterpart to the limitations of DFT methods, because combines the computational efficiency of the tight-binding methods with a parametrization that is less empirical and more straightforward to the DFT calculations.

2. The crystal structure
The crystal structure of Germanium monosulfide monolayer (GeS) is illustrated in Figure 1(a). The monolayer has four atoms per unit cell, two of each species. Each atomic species is covalently
bonded to three neighbors of the other atomic species forming a puckered structure where atoms are located on two parallel planes. As a result, \(GeS\) has an anisotropic crystal structure.

Figure 1. (a) Red (blue) balls represent S(Ge) atoms in the \(GeS\) monolayer. (b) Projection of monolayer crystal onto two-dimensional plane. Green rectangle indicates the unit cell, which contains four atoms. The zigzag and armchair edges are also indicated.

Figure 1(b) shows the projection of the \(GeS\) monolayer crystal onto the a plane. The rectangular area indicates a unit cell, which contains four atoms labeled 1, 2, 3 and 4. The corresponding lattice constants are \(a = 4.30\, \text{Å}, b = 3.65\, \text{Å}, \) and \(c = 10.44\, \text{Å},\) in \(y\) (zigzag), \(x\) (armchair) and \(z\) directions. From these atom locations, we can define the first eight lattice displacement vectors in Table 1.

Table 1. Intersite distances.

| Order | Distances between sites (Å) |
|-------|-----------------------------|
| 1     | 2.4567(1-2)                 |
| 2     | 2.4974(2-3)                 |
| 3     | 3.2043(2-3)                 |
| 4     | 3.5340(1-3)                 |
| 5     | 3.6500(2-6)                 |
| 6     | 3.8998(2-4)                 |
| 7     | 4.3000(3-7)                 |
| 8     | 4.3998(2-5)                 |

3. The tight-binding approximation
We include the \(3s\) and \(3p_{x,y,z}\) electrons in the partially filled atomic shells. The effective Hamiltonian for the monolayer is represented as the following \(16 \times 16\) matrix (Equation 1):

\[
H = \sum_{i=1}^{\alpha} \sum_{a} \left[ \varepsilon_{\alpha} c_{\alpha i}^\dagger c_{\alpha i} \right] + \sum_{j} \sum_{\beta} t_{\alpha \beta} c_{\alpha j}^\dagger c_{\beta j} + h.c.,
\]  

(Equation 1)
The inter-atomic matrix elements $t_{ss}$, $t_{s\alpha}$ and $t_{\alpha\beta}$, are initially written in terms of Slater-Koster (SK) parameters [11], as shown in equation Equation 2, with and $\alpha, \beta=x,y,z$.

$$t_{ss} = V_{ss}(d_i^n_j)$$
$$t_{s\alpha} = (d_i^m_{ij} / d_i^n_{ij}) V_{s\alpha}(d_i^n_{ij})$$
$$t_{\alpha\beta} = (d_i^m_{ij} d_j^{m\beta} / (d_i^n_{ij})^2) V_{\alpha\beta}(d_i^n_{ij}) + (\delta_{\alpha\beta} - d_i^m_{ij} d_j^{m\beta} / (d_i^n_{ij})^2) V_{\alpha\beta}(d_i^n_{ij}).$$

The inter-atomic matrix elements depend on the transfer integral between two adjacent atoms, given by $V_{lmn}(d_{ij})$, where, $l$ and $m$ are the orbital azimuthal quantum numbers $(s,p)$ of two atoms and $m$ is the common orbital magnetic quantum number $(\sigma, \pi)$. Here, $d_{ij} = (d_{nx_{ij}}, d_{ny_{ij}}, d_{nz_{ij}})$ is the inter-atomic distance and the displacement vector magnitude, given by $d_{ij} = |d_{ij}|$, are provided in Table 1. In order to limit the number of parameters, we use the semiempirical law:

$$V_{lmn}(d_{ij}) = \eta_{lmn} \hbar^2 / m_e \exp \left[ -\lambda_{lmn} \left( \frac{d_{ij}^n}{\Delta} - 1 \right) \right],$$

where $\eta_{lmn}$, $\lambda_{lmn}$ and $\Delta$ are empirically determined coefficients depending on the concerned atomic types bond, i.e, Ge $\rightarrow$ S, Ge $\rightarrow$ Ge and S $\rightarrow$ S. This definition of $V_{lmn}(d_{ij})$ (Equation 3) is similar to those used in the previous models in the literature, and is thus particularly suited for this study in order to provide an accurate representation of the band structure.

### 4. Discussion

We need to calculate three sets of coefficients ($\eta_{lmn}$, $\lambda_{lmn}$ and $\Delta$), one for each atomic types of bond and two sets of energies of the four atomic sites for each atom. These parameters are optimized to reproduce the main characteristics of the energy bands obtained from DFT calculations. We find the best set of coefficients among the 10000 generated by choosing the set that gives the lowest possible $\chi^2$ function (see Equation 4), where $\chi^2$ is just a sum of weighted squared residuals, [12] namely,

$$\chi^2 = \sum_{i=C,V} \sum_{j=1}^{N} \sigma_j^2 \left[ E_i^{TB}(j) - E_i^{DFT}(j) \right]^2.$$ 

Table 2 presents the best coefficients that we obtained using the the optimisation procedure. We can see that the hopping parameters allow a discussion on the electronic band structure of GeS, which is an indication that this model is suitable for calculations on multilayer and more complex situations which included only second nearest-neighbor interactions. Therefore, this model, with all hopping parameters, gives a good description of the electronic structure.

In Figure 2(a) we show a comparison between the band structures for a single-layer of GeS obtained with DFT and that obtained from the optimised tight-binding model described in the previous section. The optimised tight-binding model is in good agreement with the DFT results. In the band structure the model matched accurately with DFT calculations near the main gap region of the spectrum. Our optimised tight-binding model captures the energy gap, is able to describe the bands structure in the $\Gamma \rightarrow Y$ and $\Gamma \rightarrow X$ and $\Gamma \rightarrow M$ directions with high accuracy, thus allowing us to properly study the optical and transport properties.
The tight-binding model accurately predicted that the major contribution predicts about 70% contribution from $p_z$ orbitals in the conduction band, and around 90% contribution from $p_z$ for the valence band. The effective mass in the zigzag direction was found as ten times greater than that in the armchair direction, which agrees with experimental results. The next step for this model would be to investigate the effect of the anisotropy of the effective mass on electronic transport, and the effect of disorder in the system.

**Table 2.** Parameters obtained by optimization. The values are given in units of eV.

| Parameter | Ge→S       | Ge→Ge      | S→S         |
|-----------|------------|------------|-------------|
| $\eta_{ss\sigma}$ | -2.560604195 | -5.951989984 | 7.53350170  |
| $\eta_{sp\sigma}$ | -1.471195003 | -0.797606050 | -6.87549553 |
| $\eta_{pp\pi}$ | -4.669407045 | 5.231338533  | -4.502527318|
| $\eta_{pp\sigma}$ | -0.830673591 | -0.025506063 | 1.135871328 |
| $\lambda_{ss\sigma}$ | 4.353594425  | 2.939060463  | 1.250514716 |
| $\lambda_{sp\sigma}$ | 2.608255901  | 0.193011315  | 3.208444096 |
| $\lambda_{pp\pi}$ | 1.662477280  | 8.679545138  | 1.698771548 |
| $\lambda_{pp\sigma}$ | 7.764341776  | 2.651695049  | 2.005938731 |
| $\Delta (\text{Å})$ | 2.479556436  | 2.715422056  | 1.579938670 |

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**Figure 2.** Comparison between the band structures for GeS obtained with DFT (red squares) and with the optimized tight-binding model (blue circles).

### 5. Conclusion

We have developed a tight-binding model for GeS monolayer involving the effect of s-p mixing and eight neighbors in total. A high accurately describes both conduction and valence band dispersions near the high-symmetry points. We optimised the model parameters using an optimisation process of transfer integrals by Genetic algorithm and compared with the band structure obtained by density-functional theory calculation based on the hybrid HSE06 functional. We found that the band mass anisotropy is strongly manifest and should not wash away the intrinsic band structure anisotropy of this material.

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