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Electronic Structure of Surfaces in GeSe Layered Semiconductor

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Abstract

Green's function method in bases sets of Linear Combinations of Atomic Orbitals (LCAO) is used to calculate the electronic structure of the (010) surface of GeSe semiconductor. The energy states in energy gaps, their origin, orbital content, resonances and local changes in the density of states due to the surface are discussed.

Key Words: Green's function methods, Defects, Single crystal surfaces, Surface defects.

1. Introduction

The problem of the electronic structure of deep centers has been intensively studied in recent years because of their important roles in electrical and optical properties of semiconductors, the study of which can provide additional information about the optical characteristics of semiconductors. Green's function method has been shown to be a powerful tool for studying deep-level impurities, electronic structure of point defects and semiconductor surfaces.

In this paper, we have calculated the electronic structure of the ideal (010) surface of GeSe using the Green's function scattering-theoretical method. Due to the strong anisotropy of the chemical bonds and their physical properties, GeSe-type crystals have attracted considerable interest [1–3], especially for their potential applications in electronic devices.

GeSe layered compounds crystallize in the D_{2h}^{16} space group of orthorhombic symmetry, with eight atoms comprising the unit cell. The structure consists of two layers, each containing two double-corrugated planes of cation and anion atoms. Two nearest neighbors of the cation (anion) are situated on these corrugated planes, and the third nearest neighbor is situated on the next corrugated plane (010); see Figure 1 for a visual description. The layers of covalently bonded Ge-Se pairs interact weakly and can be easily cleaved along the layer planes.

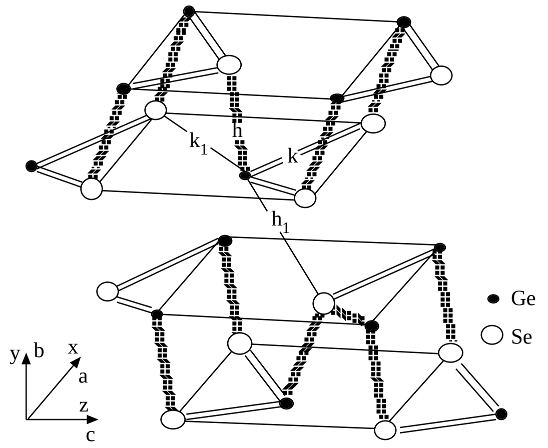

Figure 1. The unit cell of the GeSe-type compounds.

The crystal structure [4], growth, band structure and optical properties [5–7] of GeSe single crystals have been investigated in detail.

The unit cell parameters are $a = 3.82$ Å, $b = 10.79$ Å, and $c = 4.38$ Å; the coordinates of the atoms are

$$\pm\,(1/4,\ \ y,\ \ z)\,;\quad \pm\,(1/4,\ \ 1/2+y,\ \ 1/2-z)\,;$$

and the positional parameters of the cation and anion are, respectively, $y_{Ge} = 0.879$, $z_{Ge} = 0.106$ and $y_{Se} = 0.148$, $z_{Se} = 0.503$ [8]. h =2.54 Å, $k = 2.58$ Å, $h_1 = 3.39$ Å, $k_1 = 3.30$ Å are distances to the nearest six neighbors in lattice (see Figure 1).

2. Green's function method

Green's function method used in this paper was reported in [9]. Here, we only summarize its main equations.

Let H° be the perfect crystal Hamiltonian, U be the defect potential and $H = H^\circ + U$ is the one-electron Hamiltonian for the perturbed system. The one-particle Green's operator G° defined by

$$G^\circ(E) = \lim_{\varepsilon\to 0+} \left(E - H^\circ + i\varepsilon\right)^{-1},$$

and the Green's operator G defined by

$$G(E) = \lim_{\varepsilon\to 0+} \left(E - H^\circ + i\varepsilon\right)^{-1}$$

in terms of H are related by Dyson's equation

$$G = G^\circ + G^\circ U G.$$

This equation can be solved formally to obtain

$$G = \left(1 - G^\circ U\right)^{-1} G^\circ.$$

The eigenvalues of H° correspond to the poles in $G^\circ(E)$, while H has eigenvalues at energies for which H° has eigenvalues and at energies where $\left(1 - G^\circ U\right)^{-1}$ has poles in the energy gaps.

From the above equations, one can deduce [9] the following two points. (1) The states in the band gaps are given by the equation

$$\left[1 - G^\circ(E)U\right]\ \Psi = 0,$$

where Ψ is wave function of the perturbed system. Bound states correspond to the zeros of the determinant

$$D(E) = det \left\| 1 - G^{\circ}U \right\| = 0$$

(2) The state-density changes within the band continua are given by

$$\Delta N(E) = \frac{1}{\pi}\frac{d\delta(E)}{dE},$$

where

$$\delta(E) = -\tan^{-1}\left[ImD(E) \ / \ ReD(E)\right].$$

3. Energy levels of bound surface states

In order to calculate the band structure of the perfect crystal, we use a set of LCAO's constructed from the s- and p- atomic-like orbitals and then the same set of orbitals was used for the defect calculation. The values of the resonance integrals were taken from [10]. These values were then improved by fitting our band structure calculation results with previous calculations [6] and photoemission data [11–13] (see Table).

Table. Matrix elements (in eV) between atomic orbitals.

	Bond length (Å)	ssσ	spσ	ppσ	ppπ	E_s	E_p
Ge-Se (k)	2.54	−1.25	2.10	2.16	−0.73		
Ge-Se (h)	2.58	−1.25	2.10	2.16	−0.73		
Ge-Se (k_1)	3.30	−0.196	0.19	0.094	−0.06		
Ge-Se (h_1)	3.39	−0.186	0.18	0.086	−0.057		
Ge						−6.5	0.0
Se						−12.5	−1.7

Here we retain only first-, second-, third- and fourth-nearest-neighbor interactions and neglect all overlap matrix elements.

The unit cell and the irreducible part of the corresponding two-dimensional Brillouin zone constructed on the vectors $g_1 = (2\pi/a, \ 0, \ 0)$ and $g_2 = (0, \ 0, \ 2\pi/c)$ of the GeSe-type compounds are shown in Figure 1 and Figure 2, respectively. The y-axis is perpendicular to the layers. The two-dimensional unit cell for (010) surface contains one atom in each Ge and Se layer.

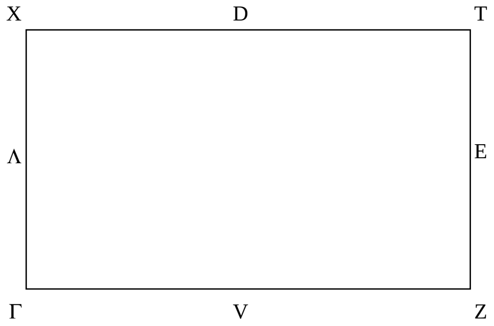

Figure 2. The irreducible part of the (010)-surface Brillouin zone of GeSe-type compounds.

The results from calculation of the projected band structure (or PBS, the projection of the bulk bands E_{nk}, with $\mathbf{k} = (\mathbf{q}, k_{\perp})$ for each $\mathbf{q}$ in the surface Brillouin zone) for GeSe is illustrated in Figures 3 and 4. In accordance with photoemission spectra [11–13], the projected valence bands of GeSe is split into three groups. The lower valence bands situated near -14 to -15 eV lies remote from others and originate from s-states (Se 4s-state). The next group of valence bands situated near -6 to -8 eV originates from Ge 4s-states and Se 4p-states. The upper part of the PBS results mainly from the Se p-states and to a lesser extent from Ge p-states; while the six lower conduction bands originate mainly from the Ge p-states and to lesser extent from Se p-states.

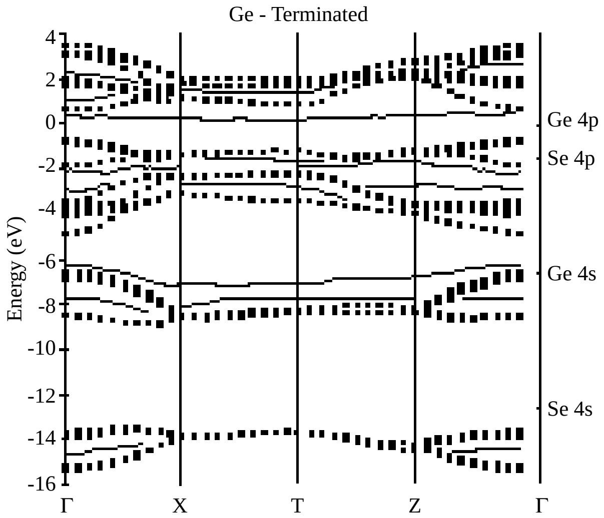

Figure 3. Projected bulk band structure and surface band structure for the Ge-terminated (010) surface of GeSe. The zero of the energy scale corresponds to the Ge 4p level.

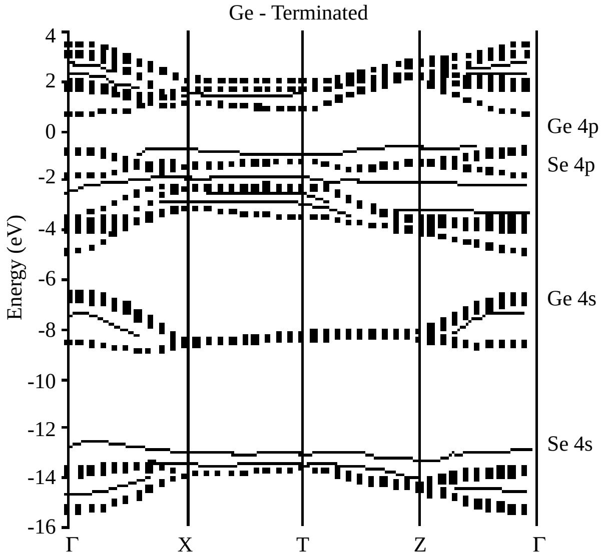

Figure 4. As in Figure 3, but for Se-terminated (010) surface of GeSe.

As one can see from PBS, the dispersion along the direction perpendicular to the layer is small and the band structure with different $k_\perp$ slightly differs from each other because of the interlayer interactions in GeSe is very weak.

We now use the “atom-removal method” described in [9] to examine the surface band structure. As mentioned above, two nearest neighbors of the cation (anion) are situated on the same corrugate planes, and the third nearest neighbor is situated on the next corrugated plane (010): therefore the creation of the surface can be accomplished by removing a cation or anion containing layer in the fourth-nearest-neighbor interactions. The creation of two adjacent Ge- (Se-) terminated surfaces is accomplished by removing one Se (Ge) layer yielding a 4×4 Green's-function matrix. In Figure 3 and Figure 4, one can see the gaps and "pockets" where bound states at the surface should be calculated. The condition for the existence of bound states in the gaps and pockets of the PBS is given in [9] (see equation B1 therein):

$$\tilde{D}(E) = det\left\|G^{\circ}_{m,m'}\right\| = 0,$$

where the indices m and m‘ run over one layer at the Ge (Se)-terminated surface. The surface band structure are shown in Figures 3 and Figure 4 as solid lines.

The details of the calculation of the wave function, the change in the density of states induced by surface and local densities of states on each layer are described in [6]. Figures 5 and Figure 6 show the wave-function amplitudes summed over the s- and p- orbitals for some surface states on the first 10- layers for the Ge- and Se- terminated surfaces defined in [9] (equation (28)):

$$f^{m}_{sq}(E_s) = \sum_{\alpha}\left\|A^{m,\alpha}_{s,q}(E_s)\right\|.$$

The presence of surface results with these bound states appears in the gap and the densities of states within the band continua vary. In Figures 7 and Figure 8 we give the local density of states (DOS), the change in the local DOS and the total change at the first six layers for the Ge- and Se- terminated surfaces, respectively. From these figures, we see that almost all bound states are highly localized; and, effectively after the third layer, the local DOS becomes almost identical with the layer density of states in the bulk infinite crystal. This is a consequence of the fact that separate layers in GeSe are situated far from each other.

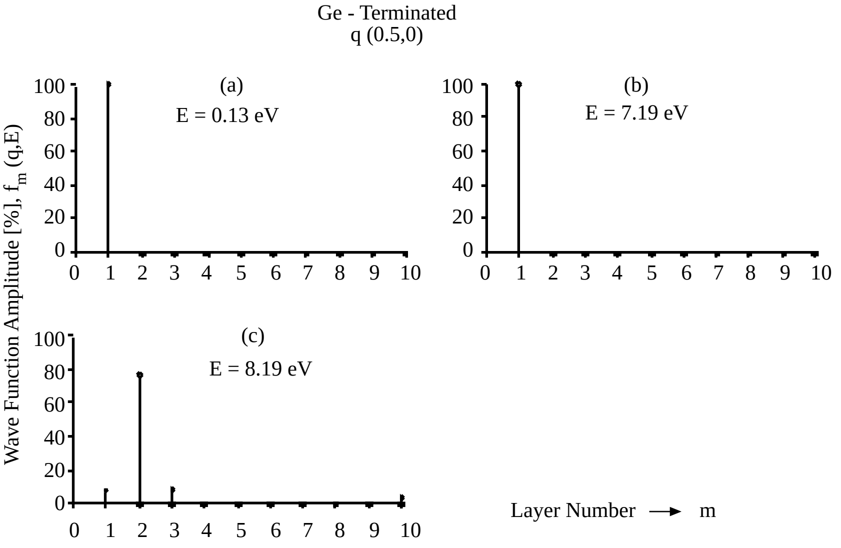

Figure 5. Wave-function amplitudes summed over the s- and p-orbitals as a function of the layer number for surface states for the Ge-terminated (010) surface.

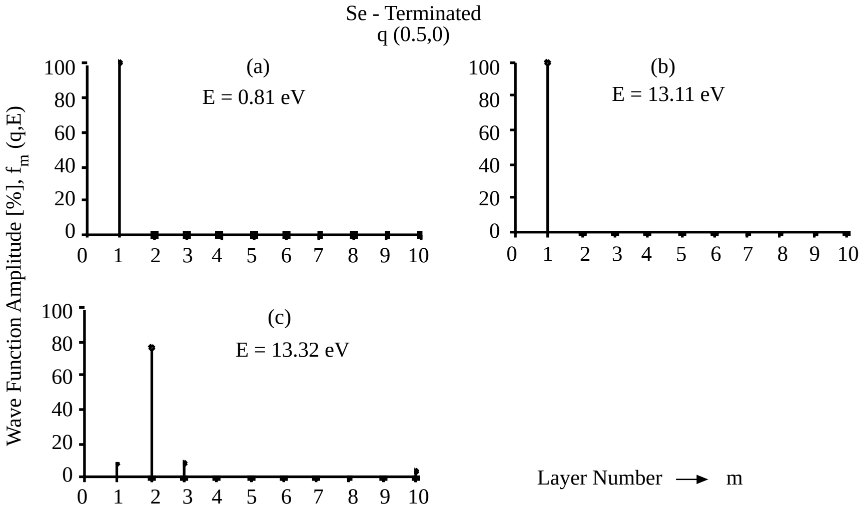

Figure 6. As Figure 5, for the Se-terminated (010) surface of GeSe.

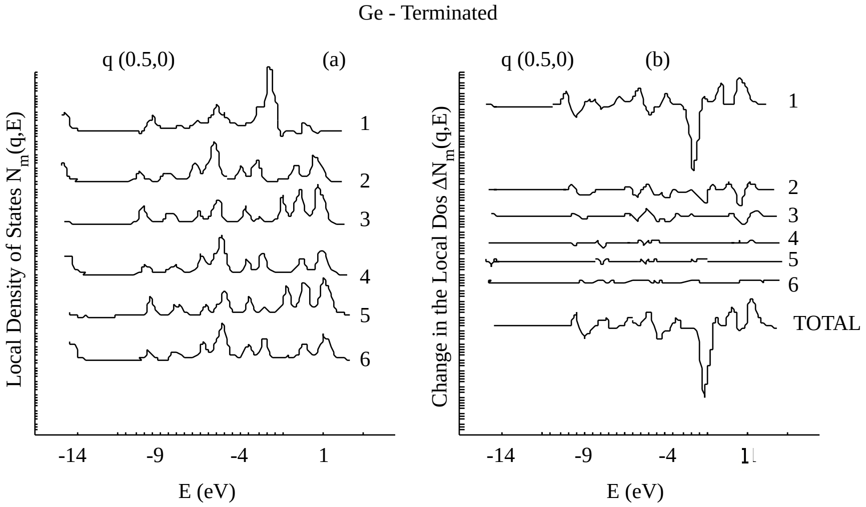

Figure 7. (a) Local densities of states at each of the first six layers for the Ge- terminated (010) surface of GeSe at the symmetry point X of the surface Brillouin zone. (b) The changes in local density of states at each of the first six layers.

The total changes in the local density of states for each layer are shown in Figures 7 and Figure 8 where the resonances, antiresonances and wave-function localization are observed for each case.

Both Ge- and Se terminated surfaces have surface states in pockets around -14.5 eV and -7.5 eV. These states localized on the two layers show similar dispersion and derived totally from the valence states.

There are two surface states predominantly localized on the Se 4s orbitals around -13 eV; and there are two surface states localized on the Ge s orbitals around -7 eV for the Se- and Ge- terminated surfaces, respectively. It once more confirms that the character and energetic position of most surface states depend on the nature of atoms in the first layer. An orbital decomposition of wave-function amplitude, dependence of local densities of states and changes in the local DOS (Figure 7 and Figure 8) as a function of the layer number shows that the surfaces states around -13 eV for Se-terminated surface are highly localized within three layers and are predominantly anion s-like. The surface states around -7 eV for Ge-terminated states are also highly localized within three layers and formed by s- and p_x- orbitals. This is consistent with the fact that the bulk valence bands are dominated by anionlike states around -14 eV and cationlike states around -7 eV.

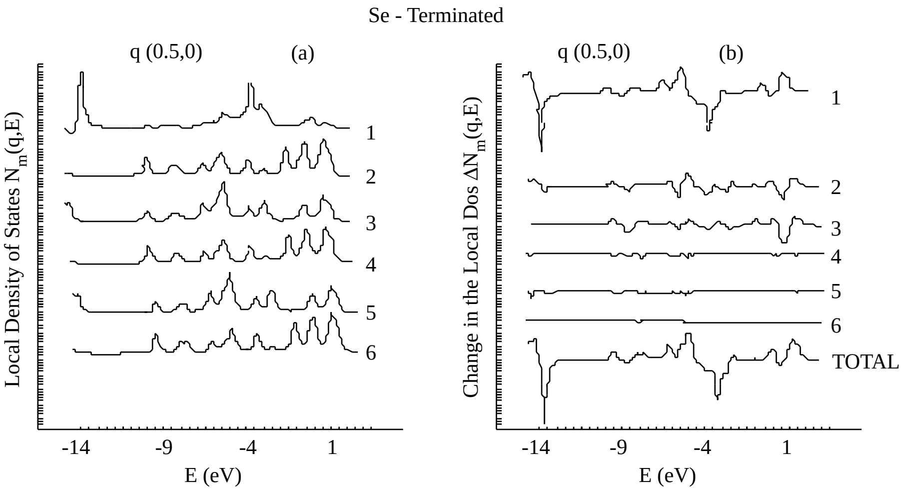

Figure 8. As Figure 7, for the Se-terminated (010) surface of GeSe.

As shown in Figures 3 and 4, one bound surface state was found in the band gap for both surfaces. The surface state in the fundamental gap for the Ge-terminated surface is almost dispersionless, whereas the surface state for the Se-terminated surface lies very close to the bulk valence bands and shows similar dispersion.

We investigate the origins of the surface state for Se-terminated surface in the fundamental gap integrating $\Delta N(E)$ at $q(0.5,\ 0,\ 0)$ over the projected valence bands defined by,

$$\int_{E_{bot}}^{E_{top}} \Delta N(E)\,dE = \frac{2}{\pi}\left[\delta(E_{top}) - \delta(E_{bot})\right],$$

where E_{bot} and E_{top} are the bottom and top of the valence bands.

We find that a total one state has been removed, indicating that the surface state in the fundamental gap is mainly derived from the valence bands. Similarly, in order to carry out integration $\Delta N(E)$ over the projected conduction bands for Ge-terminated surface, we reveal that a total one state has been removed, indicating that the surface state in the fundamental gap is mainly derived from the conduction bands and not occupied by electrons.

To determine the surface states of occupation in the forbidden gap, it is enough to know $\Delta N(E)$ and number of electrons introduced by the defect. At removal atom Se, a valence band leaves 6 electrons and one valence state moves to the forbidden gap. Therefore, a surface state appears empty and the conductivity of a surface has semiconductor character. Appearance of empty states in the band gap strongly influences optical and electrical properties of semiconductors as donor and acceptor levels. In semiconductors at low temperatures in view of strong falling of carrier concentration in the conduction bands the role of charge transport by hopping on the local states sharply rise.

The wave function amplitude (Figure 5 and Figure 6) shows that these states are completely localized in the surface plane. An orbital decomposition of the wave-function amplitude for these states shows that both these states are primarily p_z-like with a small s-like admixture and acts like a link between surface atoms.

4. Conclusion

Green's function method is used to calculate the electronic structure of the (010) surface of GeSe semiconductor. We use a set of LCAO's to form Bloch sums and expand the crystal wave function in terms of these Bloch sums. The results for the Ge- and Se-terminated (010) surfaces of GeSe show that there is one bound surface state in the fundamental gap for both surfaces. We obtain that these states are completely localized in the surface plane and are primarily p_z-like with a small s-like admixture and act like a link between surface atoms.

The defect-induced change in the density of states $\Delta N(E)$ is calculated. Furthermore, several resonances and antiresonances within the valence bands which associated with the surface are obtained.

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