THE INVESTIGATION OF THE ELECTRON STRUCTURE OF THE (010) GeSe SURFACE BY GREEN FUNCTION METHOD

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The electron structure of (010) surface, limited by Ge atoms in the layered semiconductor GeSe has been considered on the base of Green function theory in the basis of Linear Combination of Atom Orbitals (LCAO). The electron states in the forbidden band, resonances and change of the density of energy states in crystal, connected with the defect have been discussed.

Introduction

The study of the electron structure of deep defect centers plays the important role in the understanding of electric and optic properties of semiconductors. It is shown, that the electron properties of semiconductor devices are especially sensitive to the character of the different defects and their concentration. Last years, Green function method is the one of the main methods of the defect studying with deep energy level, electron structures of the point defects and semiconductor surfaces.

The semiconductor compound GeSe is related to the layered semiconductors by A^4B^6 group [1-5]. The layered structure of the crystals, caused by anisotropy in chemical connections of atoms, from which the quasi-two-dimensional crystal lattice is built, is the main their peculiarity. The unit cell consists from the two layers, each layer includes two molecules, where the atoms of the neighbor layers are connected by weak Van-der-Waals forces between themselves and as the result, some physical properties of these crystals have two-dimensional character. In this work the electron structure of (010) surface, limited by Ge atoms of semiconductor compound GeSe is calculated by Green function method.

The crystal structure [4], electron structure and optical properties [6,7] of GeSe compound are well studied.

Green function method.

Green function method is well described in [8]. Here we give the main equations of this method. Let's H_0 is effective one-electron Hamiltonian of ideal crystal, U is defect potential, and $H=H_0+U$ is Hamiltonian of perturbed system. Then, the one-particle Green operator of ideal crystal

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

And Green operator of perturbed system

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

Are connected between each other by Dawson equation:

$$G = G^0 + G^0 U G$$

The formal solution of this equation for G is:

$$G = (1 - G^0 U)^{-1} G^0$$

The energy levels of perturbed system correspond to poles of G function. We obtain the following for the levels in the forbidden band:

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

Ψ is wave function of perturbed system. The connected states correspond to determinant zero:

$$D(E) = Det\| 1 - G^0 U \| = 0.$$

The change of the density of electron states is defined by the formula:

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

Here,

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

Energy levels of connected states.

The LCAO, constructed from s- and p-orbitals was used for the definition of band structure of ideal crystal and then the same set was used for the calculation of localized states. The values of resonance integrals were taken from [9]. Further, these data became better by the way of the picking out of our results on the band structure with the previous calculations and with experiment data on photoemission [10].
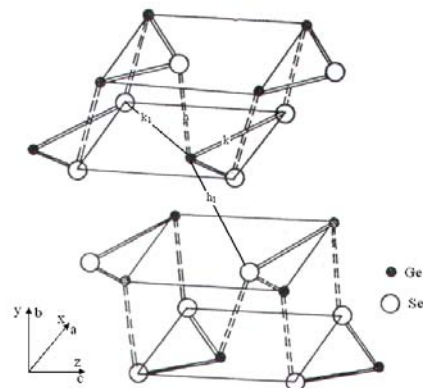

Fig. 1. Unit cell of GeSe-type compounds.

In calculations we took under consideration the contributions of only first four neighbors. The unit cell of the compounds by GeSe type is shown on the fig.1. *Y* axis is perpendicular to the crystal layers. The two-dimensional cell for (010) surface has one Ge atom and one Se atom in each layer. The

calculation results of projected band structure GeSe (PBS is E_{nk} projection of infinite crystal with $k=(q, k_\perp)$ for each q in two-dimensional 3B) are shown on the fig.3. The projected valency band consists from three groups in the correspondence with photoemission spectrum [10]. The lowest group, situated in energy interval –14-15 eV, is far from others by wide energy gap and it comes from s-states (Se 4s). The next group in 6-8 eV interval comes from 4s-states of Ge and 4p-states of Se. The upper group of PBS mainly comes from p-states of Se and in lesser extent comes from p-states of Ge, at the same time the situation is vice versa for the six lowest conduction bands.
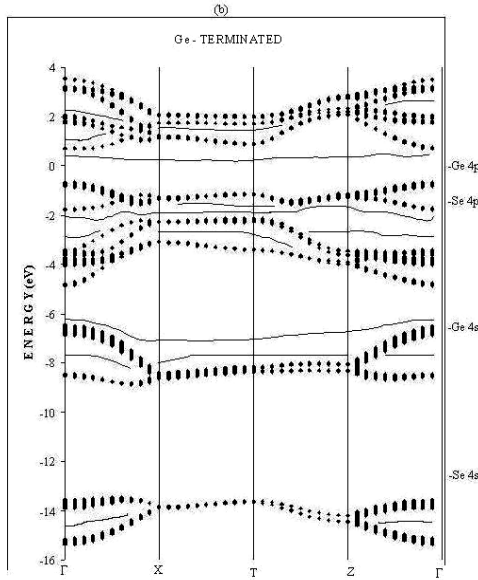

Fig.2. Projected bulk band structure and surface band structure for the Ge- terminated (010) surface of GeSe

In GeSe crystal the two nearest neighbors of cation (anion) situate on the one crimped plane, third nearest neighbor situates on the next crimped plane (010), that's why it is enough to delete plane having the cation (anion) with taking into consideration of interaction deposit of fourth nearest neighbor for the creation of the free surface. The one plane, having Se atoms, is deleted, the surface, limited by Ge atoms, is created. The chinks and "pockets", where it is need to calculate the localized states is well seen on the fig.2. The existence conditions of localized state ([8], (B1)]).

$$D(E) = Det// G^0_{m,m`} // = 0 \ ,$$

Where indexes m and m' run on the s- and p-orbitals of the atom of deleted level. The surface band structure and localized states are shown on the fig.2. The amplitudes of wave functions, summed on s- and p-orbitals for the some surface levels for first ten layers with the help of formula ([8], (28)]) are shown on the fig.3.

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

The presence of the surface leads to the appearance of localized levels in forbidden band, and in permitted band the density of energy states changes. The local state density, the change of local state density, total change of state density on the first seven layers for the surfaces, limited by Ge atoms,

are shown on the fig.4. It is seen from the figure, that in practices all surface states are strongly localized and in practices after third layer the local state density becomes an identical one with density of electron states of infinite crystal.

The common changes of local state density for each layer, where the resonances, anti-resonances and localization of wave function for each case are well seen, are shown on the fig.4. As it is seen from the fig.2 the surface states near –14,5 eV and –7,5 eV, which are localized in the limits of two layers and come from valency states, are present. Besides, two surface states near s-states of Ge near –7 eV are present. This shows that the character and energy situation of many surface states depend on atom nature on the first level.
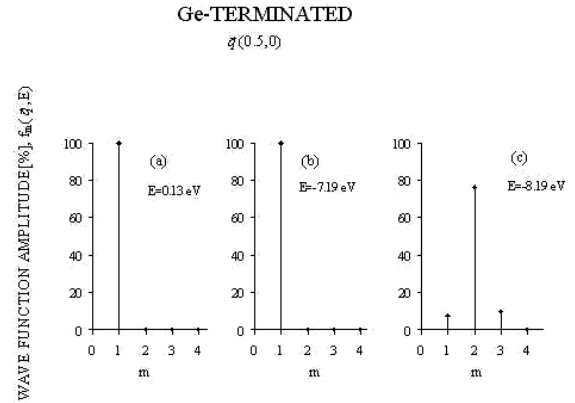

Fig.3. Wave-function amplitudes summed over the s- and p-orbitals as a function of the layer number for surface states for the Ge- terminated (010) surface of GeSe
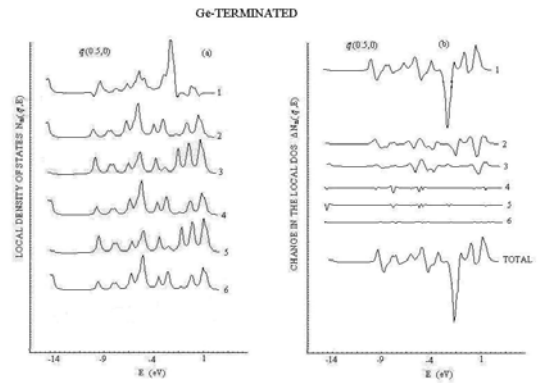

Fig. 4. (a)- Local densities of states at each of the first six layers for the Ge- terminated (010) surface of GeSe at the symmetry point X of the surface Brillouin zone
(b)- The changes in local density of states at each of the first six layers

The orbital situation of amplitudes of wave functions, the dependence of local densities of energy states on the level numbers show, that surface state near –7 eV is localized in the limits of three layers and is formed from s- and формула-orbitals. This well corresponds with the fact, that valency band near –7 eV mainly comes from cation states. As it is seen from the fig.2 in forbidden band the one almost dispersion-free localized state takes place. We have been integrated $\Delta N(E)$ in $q(0.5, 0.0)$ on projected valency band for the occurrence investigation,

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

Where E_{bot} and E_{top} are bottom and top of valency band. We have been revealed, that the one state in conduction band is chipped off in the forbidden band because of the presence of the surface. This shows, that local state in forbidden band comes from conduction band. The orbital situation of amplitudes of wave functions of this state shows, that this state mainly is p_z - typed one with small s-typed impurity and does as the connecting bridge between atoms of neighbor layers and totally is localized in surface plane.

Conclusion.

The electron structure of (010) surface, limited by Ge atoms in layered semiconductor GeSe has been considered on the base of Green function theory in basis of Linear Combination of Atom Orbitals. The calculation results show, that the presence of the surface leads to the appearance of one surface level in fundamental forbidden band. It is established, that this level is totally localized in surface plane, is p_z -typed level with small s-typed impurity and connects atoms of neighbor planes. Besides, the $\Delta N(E)$ -change of density of electron states, inducted by defect, and also the resonances and antiresonances, connected with surface presence, have been calculated.

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QRİN FUNKSİYASI METODU İLƏ GeSe YARIMKEÇİRİCİSİNİN SƏTH ELEKTRON STRUKTURUNUN HESABLANMASI

Qrin funksiyası nəzəriyyəsi vasitəsilə Atom Orbitallarının Xətti Kombinasiyası bazisində GeSe laylı kristalının Ge atomları ilə məhdudlaşan (010) səthinin elektron quruluşu təyin edilmişdir. Qadağan zolağında yerləşən enerji səviyyəsi, rezonanslar və defektin təsirilə enerji səviyyələri sıxlığının dəyişməsi müzakirə olunmuşdur.

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РАСЧЕТ ЭЛЕКТРОННОЙ СТРУКТУРЫ ПОВЕРХНОСТИ В GeSe МЕТОДОМ ФУНКЦИИ ГРИНА

На основе теории функции Грина в базисе линейной комбинации атомных орбиталей (ЛКАО) рассмотрена электронная структура поверхности (010), ограниченная атомами Ge в слоистом полупроводнике GeSe. Обсуждены электронные состояния в запрещенной зоне, резонансы и изменение плотности энергетических состояний в кристалле, связанные с дефектом.