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Vasyl Stefanyk Precarpathian National University

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O.O. Spesyvykh[1], T.M. Zajac[1], I.M. Yurkin[1], I.I.Nebola[1], M.M.Pop[1,2], V.M. Rubish[1,2]

Research of energy structure of crystalline compounds in Ag(Tl)-As(P)-S(Se) systems

[1]*Uzhgorod National University, Uzhgorod, Ukraine,*
[2]*Institute for Information Recording, NAS of Ukraine, Uzhgorod Ukraine,* center.uzh@gmail.com

The paper presents the results of studying the peculiarities of formation of the valence band and the conduction band of crystalline compounds in Ag(Tl)-As(P)-S(Se) systems with sp^3-type bond by using the photoelectron spectroscopy method. From the spectral distribution of photoemission by energy, the crystal photoelectron work function $h\nu_0$ was determined. It was shown that the use of a limited basis (only ionization potentials of atoms and interatomic distances) for crystals with sp^3-type bond within the framework of the LCAO model gives sufficiently accurate results of the position of the valence band top and the electron affinity value. Calculations show that the position of the valence band top defines the bonds of As-S(Se) and P-S(Se) atoms, while the hybridized orbitals of Ag and Tl atoms are formed in the conduction band.

Keywords: photoemission threshold, semi-empirical calculations, valence band, conduction band, Fermi level, electron affinity.

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Introduction

When certain concentrations of silver or thallium are introduced into the composition of compounds of binary systems As(P)-S(Se) (for example, As_2S_3, As_2Se_3), formation of new ternary crystalline compounds is possible (for example, $AgAsS(Se)_2$, $TlAsS(Se)_2$, $Tl_3As(P)S(Se)_4$) with unique properties that can be used as active elements for devices of micro- and nanoelectronics, optics and optoelectronics [1-10].

The atomic structure of these materials is studied in detail in [1, 2, 8, 11-15]. The analysis of these works showed that when Ag or Tl is introduced into the composition of arsenic or phosphorus chalcogenides due to the transfer of valence electrons to sulfur or selenium, structural units of different shapes can be formed: from chain ones for $As_2S(Se)_3$, $AgAsS(Se)_2$, $TlAsS(Se)_2$, to trigonal (for $Ag_3AsS(Se)_3$ and $Tl_3AsS(Se)_3$) and tetragonal (for $Tl_3As(P)S(Se)_4$) pyramids. However, in all cases the sp^3-type bond is preserved. The As-S interatomic distances are 1.93 – 2.59 Å.

The minimum interatomic distances of Tl-S in $TlAsS_2$ (2.97 Å) and T_3AsS_4 (3.03 – 3.52 Å) are significantly larger than the sum of their covalent tetrahedral radii (2.48 Å). The interatomic distances in Tl_3AsSe_4 are equal to 3.18 Å, while the minimum Tl-Se distances are 2.58 Å. According to the analyzed data, it can be concluded that the structure of the studied crystalline compounds can be presented in the form of molecular complexes S(Se)-As(P)-S(Se), As-3S(Se) and As(P)-4S(Se), connected by silver or thallium atoms.

If the structure of crystalline compounds in Ag(Tl)-As(P)-S(Se) systems is well studied, the mechanism of formation of their electronic spectrum is not sufficiently studied, which somewhat restrains the wider practical application of these materials. Knowledge of the peculiarities of formation of the zonal structure makes it possible to modify it for specific requirements. One of the most important parameters of semiconductor materials is the position of the Fermi level (E_F), which determines the contact potential difference when constructing the electronic devices, the position of the top energy of the valence band, and the value of the electron affinity (χ).

This work is devoted to the study of the spectral distribution of photoelectrons and to determination of the features of formation of the valence band and the conduction band of crystalline compounds with *sp*^{3}-type bond in the Ag(Tl)-As(P)-S(Se) systems.

I. Methodology of the experiment

Investigations of the spectral distribution of photoelectrons Y(*hν*) of crystalline compounds of the A^VB^{VI}-Ag(Tl) (A^V-As, P; B^{VI}-S, Se) system were carried out at the energies of incident photons of 4.5 to 7.0 eV. Radiation is obtained by electric discharge in hydrogen. A 0.5 m Seiya-Namioki monochromator with a diffraction grating of 1200 lines per mm was used. Registration of photoelectrons was carried out with the secondary electronic multiplier VEP-6. The sensitivity was $(1\ldots3)\cdot10^{-19}$ A. The accuracy of determining the photoemission threshold is no worse than ±0.1 eV. Vacuum in the measuring chamber ~ $5\cdot10^{-7}$ mm Hg.

The energy position of the valence band top (photoelectron work function $h\nu_0$) was determined by using the extrapolation of the near-threshold area of the spectral distribution of the quantum yield of photoemission $Y^{1/3}(h\nu)$.

II. Experimental and calculation results

The dependences of $Y^{1/3}(h\nu)$ in arbitrary units are shown in Fig. 1. The presence of straight sections in these dependences may indicate the indirect nature of photoelectron excitation. Note that the $Y^{1/3}(h\nu)$ dependences for $TlAsS_2$ and Tl_3AsS_3 compounds almost perfectly match. The results of measurements and calculations of the parameters of the energy spectra of compounds in the As(P) – S(Se) – Ag(Tl) systems are listed in Table 1. It can be seen that as compared to As_2S_3, for which $h\nu_0$ = 6.2 eV, three-component compounds, containing As, P, S, Ag, and Tl, have significantly lower values of the photoelectron work function. For the compounds $AgAsS_2$ and Ag_3AsS_3, the $h\nu_0$ values are taken from the work [17].

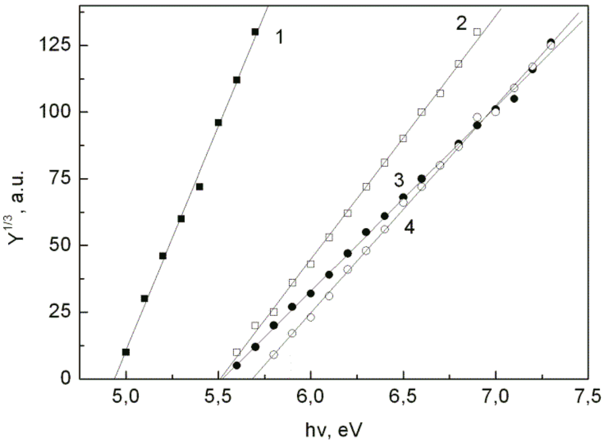

Fig. 1. Dependence of $Y^{1/3}(h\nu)$ for the Tl_3PSe_4 (1), Tl_3AsS_2 (2), Tl_3PS_4 (3), Tl_3PS_4 (4) crystals.

The position of the Fermi level E_F and the value of the electron affinity χ were determined from the expressions:

$$E_F = h\nu_0 - \frac{E_g}{2} \quad (1)$$

$$\chi = h\nu_0 - E_g \quad (2)$$

Table 1.

Parameters of the energy spectrum of crystalline compounds in Ag (Tl)-As(P)-S(Se) systems

Compound	E_0, eV (*)	$d_{cor.E0}$, Å	$h\nu_0$, ±0.1 eV	E_g,±0.1 eV	$d_{cor.E1}$, Å	E_1, eV	χ, ±0.1 eV	E_F, ± 0.2 eV
As_2S_3	5.8	2.155	6.2	2.36	-	-	3.84	5.0
As_2Se_3	5.1	2.20	5.6	1.6	-	-	4.0	4.8
$AgAsS_2$	5.8	2.19	5.9	2.2	2.56	3.7	3.7	4.8
$AgAsSe_2$	5.1	-	-	1.95	2.54	3.34	3.37	4.1**
Ag_3AsS_3	5.8	2.19	5.9	2.2	2.56	3.7	3.7	4.8
Ag_3AsSe_3	5.1	-	-	1.23	2.64	3.44	3.47	4.1**
$TlAsS_2$	5.8	2.31	5.5	1.8	2.72	3.7	3.7	4.6
$TlAsSe_2$	5.1	-	-	1.36	2.60	3.5	3.5	4.2**
Tl_3AsS_3	5.8	2.31	5.5	1.6	2.59	3.9	3.9	4.7
Tl_3AsS_4	5.8	2.31	5.5	2.06	3.03	3.4	3.4 4	4.5
Tl_3AsSe_4	5.1	-	-	1.38	2.502	3.72	3.72	4.4**
Tl_3PS_4	6.3	2.25	5.7	2.48	3.380	3.22	3.22	4.46
Tl_3PSe_4	5.5	2.38	4.9	1.46	2.645	3.4	3.44	4.2

Note:

(*) – the sum of the covalent tetrahedral radii of atoms, the values of which are given in Table 2, was used in the calculation.

(**) – when calculating the position of the Fermi level, the work function value E_0 was used.

In these expressions, E_g is the band gap width of crystals. In the absence of data on photoemission ($h\nu_0$), for compounds $AgAsSe_2$, Ag_3AsSe_3, $TlAsSe_2$, Tl_3AsSe_4, the Fermi level was estimated from the expression $E_F = h\nu_0 - \frac{E_g}{2}$. The E_g values of the studied compounds are given in [18] and are listed in Table 1. As can be seen from Table 1, the values of E_F and χ are within 4.1 – 5.0 eV and 3.2 – 4.0 eV, respectively. Note that the Fermi level for selenide compounds is 4.1 – 4.4 eV (the exception is As_2Se_3), and for sulfide compounds it is 4.5-5.0 eV. The results of determining the position of the Fermi level correlate well within the accuracy of the experiment with the results given in [19].

Note that information on the structure of the energy spectrum of crystalline compounds in the Ag(Tl)-As(P)-S(Se) systems with a sp^3-type chemical bond can be obtained within the framework of the LKAO (linear combination of atomic orbitals) model [20], in which for calculations of energy values a limited database is used – ionization potentials of atoms and interatomic distances.

According to [20], the photoelectron work function from semiconductor materials with a sp^3-type chemical bond can be described by the expression:

$$E_{0,1} = \frac{1}{2}(\varepsilon_h^c + \varepsilon_h^a) - (V_2^2 + V_3^2)^{1/2} - V_1 - \Phi_0 \qquad (3)$$

where E_0 is the photoelectron work function for the As(P)–S(Se) complexes; E_1 – photoelectric work function for Ag(Tl)-S(Se) complexes; ε_h^c, ε_h^a – energies of hybridized sp^3 states of cation and anion, respectively; Φ_0 is an additive constant, the value of which for many semiconductors is equal to 3.8 eV; V_1^a and V_1^c – matrix elements that describe transitions within the orbitals of anion and cation and characterize the energy of metallic bond; V_2 – matrix element that describes transitions from the anion orbital to the nearest orbital of cation and characterizes the energy of covalent bond; V_3 – matrix element that characterizes the energy of ionic bond.

The values of the matrix elements V_1^a and V_1^c, V_2 and V_3 were given by the expressions [20]:

$$V_1^{a,c} = \pm(\varepsilon_p - \varepsilon_s)/4 \qquad (4)$$

$$V_2 \sim 39.5 \cdot d^{-3} \qquad (5)$$

$$V_3 = \pm(\varepsilon_h^c - \varepsilon_h^a)/2 \qquad (6)$$

In these expressions, ε_p and ε_s are the ionization potentials of the *p* and *s* orbitals of atoms of cation or anion [21]; *d* is the interatomic distance in Å. The energies of the hybridized states of anion or cation were determined from the expression:

$$\varepsilon_h^{a,c} = \frac{(\varepsilon_s + 3\varepsilon_p)}{4} - \frac{14.4}{4 \cdot d} \qquad (7)$$

In this work, for calculations of E_0 and E_1, which were performed separately for the As(P)-S(Se) and Ag(Tl)-S(Se) complexes, the sum of the tetrahedral radii of atoms (*r*) was taken as the interatomic distances *d*. The *r* values of atoms given in Table 2, were taken from the work [22]. The same table also shows the values of the ionization potentials ε_p and ε_s.

Table 1 shows that for the binary compounds As_2S_3 and As_2Se_3 and for the ternary compounds $AgAsS_2$ and Ag_3AsS_3, the values of the calculated work function E_0 are smaller than the values of the photoelectronic work function $h\nu_0$. For the compounds, containing thallium and phosphorus, $E_0 > h\nu_0$. Such a difference in the E_0 and $h\nu_0$ values of As(P)-S(Se) complexes may be related to the fact that the interatomic distances in real crystals do not always correspond to the sum of the tetrahedral radii of atoms. Accordingly, there is also a difference in the values of the calculated bond energies E_1 of the Ag(Tl)-S(Se) complexes.

The deviation in the *d* values, determined from the data of X-ray structural analysis and obtained by summing up the tabular radii of atoms, can be both higher and lower. To determine the value of this deviation, E_0 and E_1 were calculated for different values of interatomic distances *d*. The dependences of $E_0(d)$ and $E_1(d)$ are shown in Fig. 2. It can be seen that the values of E_0 and E_1 depend significantly on the interatomic distances. Using the $E_0(d)$ and $E_1(d)$ dependences and the experimental values of the photoelectron work function $h\nu_0$ of the compounds, the corrected distances $d_{cor.E0}$ and $d_{cor.E1}$ were determined for the As(P)-S(Se) and Ag(Tl)-S(Se) complexes, respectively. The values of $d_{cor.E0}$ and $d_{cor.E1}$ are listed in Table 1.

From a comparison of the data in Tables 1 and 2, it can be seen that the values of the corrected interatomic distances $d_{cor.E0}$ and the interatomic distances *d*, obtained by summing up the table tetrahedral radii *r*, are slightly different. The difference in the values of *d* and $d_{cor.E0}$ also determines the difference in the values of the calculated E_0 and the experimentally determined $h\nu_0$ work functions of crystal. So, for As_2S_3, the value of the work function E_0 is 5.8 eV. This corresponds to the *d* value that is equal to 2.216 Å. The work function $h\nu$ of As_2S_3 is equal to 6.2 eV. In this case, the interatomic distance ($d_{cor.E0}$) between arsenic and sulfur atoms should be 2.155 Å.

For As_2Se_3, E_0 = 5.1 eV (d = 2.319 Å), and $h\nu_0$ = 5.6 eV ($d_{cor.E0}$ = 2.20 Å). Accordingly, the difference in the values of $h\nu_0$ and E_0 is 0.4 eV for As_2S_3 and 0.5 eV for As_2Se_3. For compounds containing silver, $d_{cor.E0} < d$, and for compounds containing thallium and phosphorus, $d_{cor.E0} > d$. For example, for compounds of the Tl-As-S system, the values of *d* and $d_{cor.E0}$ are 2.422 and 2.31 Å, respectively. For the Tl_3PS_4 compound, these values are 2.124 and 2.25 Å, respectively. The obtained experimental and calculation results make it possible to conclude that the position of the valence band top of the crystalline compounds of the Ag(Tl)-As(P)-S(Se) systems determines the bonds of the As(P)-S(Se) atoms.

Calculations of the bond energies E_1^* of Ag(Tl)-S(Se) complexes showed that if the sum of the tetrahedral radii of Ag, Tl, S, and Se atoms is chosen as the interatomic distances, then the E_1^* values are 3.8 eV for $AgAsS_2$ and Ag_3AsS_3, 3.2 eV for $AgAsSe_2$ and Ag_3AsSe_3 as well as 3.4 eV for all the compounds containing thallium in their composition.

Calculations of the bond energies E_1 of Ag(Tl)-S(Se) complexes, carried out taking the experimental results into account, indicated some difference in the values of E_1 and E_1^* (Table 1). In our opinion, it is caused by differences in the values of interatomic distances in real crystals and in the values of interatomic distances obtained by summing

Table 2.

Parameters for calculations of work function of crystals

Compound	Атом					
	P	As	S	Se	Tl	Ag
ε_s, eB	17,10	17,33	20,80	20.32	9.92	6.41
ε_p, eB	8,33	7,91	10,27	9.53	4.61	2.06
$r_{tetr.}$, Å	1,084	1.176	1.04	1.145	1.44	1.473

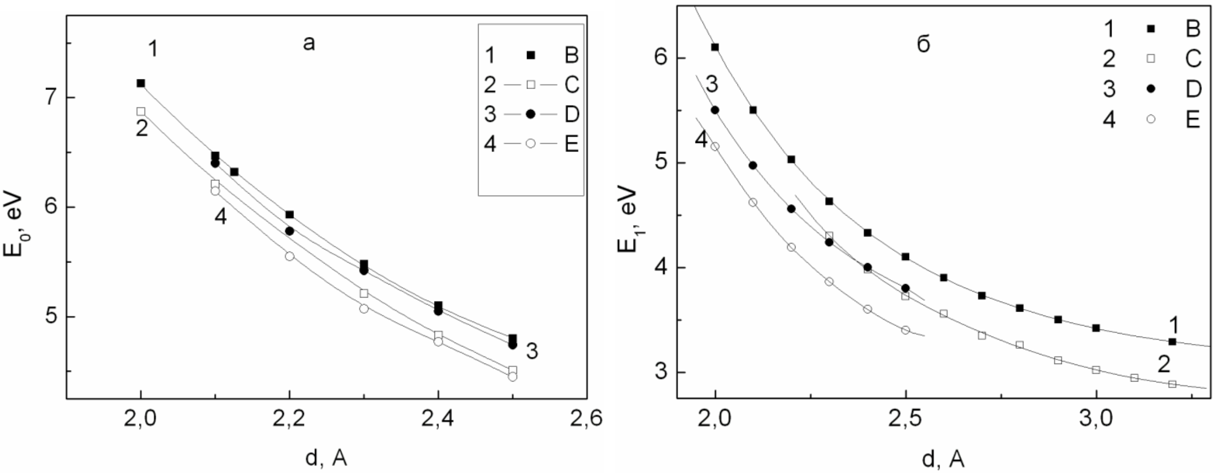

Fig. 2. Dependences of E_0 (a) and E_1 (b) on the interatomic distances: a) P-S (1), P-Se (2), As-S (3), As-Se (4); b) Tl-S (1), Tl-Se (2), As-S (3), Ag-Se (4).

the tetragonal radii of atoms (*d*). For example, for Tl-S bonds, the interatomic distances *d* are equal to 2.422 Å. The same distances for some compounds in the Tl-As-S system are within the range of 3.03 to 3.52 Å, which were determined from X-ray analysis data, as it was noted in the introduction of this work. The corrected interatomic distances $d_{cor.E1}$ for Ag(Tl)-S(Se) complexes are given in Table 1. It can be seen that depending on the chemical composition of the investigated compounds of the Ag(Tl)-As(P)-S(Se) systems, the $d_{cor.E1}$ values can be both smaller and larger than the *d* values. It is most likely that the difference in the values of *d* and $d_{cor.E1}$ is caused by the peculiarities of the atomic structure of the studied materials.

It can be seen from Table 1 that the value of the bond energy *E* of the Ag(Tl)-S(Se) complexes with the corrected interatomic distances of Ag-S(Se) and Tl-S(Se) is within 3.22 – 3.72 eV. This means that energy levels are located in the conduction band and can be defined as the levels of electron affinity χ.

Conclusions

The spectral distribution of photoemission in crystalline compounds of the Ag(Tl)-As(P)-S(Se) systems has been studied and their photoelectron work function $h\nu_0$ has been determined. It has been shown that in comparison with As_2S_3, for which $h\nu_0 = 6.2$ eV, the three-component compounds containing As, P, S, Ag and Tl, have significantly lower values of the photoelectric work function. It has been shown that the use of a limited basis (only ionization potentials of atoms and interatomic distances) for the crystals with sp^3-type bond within the framework of a semi-empirical method gives sufficiently accurate results of the position of the valence band top and the electron affinity value.

The values of work function E_0 for As(P)-S(Se) complexes and bond energy E_1 for Ag(Tl)-S(Se) complexes have been calculated. The authors have revealed the differences in the values of $h\nu_0$ and E_1 caused by the difference in the values of interatomic distances in real crystals $d_{cor.E0}$ and in the values of interatomic distances *d* obtained by summing the tetrahedral radii of atoms. It has been shown that the position of the valence band top is determined by the bonds of As(P)-S(Se) atoms, and the position of the conduction band bottom is determined by the bonds of Ag(Tl)-S(Se).

Spesyvykh O.O. – associate professor of the Department of Electronic Systems of Uzhhorod National University, a candidate in physical and mathematical sciences, docent;
Zajac T.M. – Head of the Department of Electronic Systems of Uzhhorod National University, a candidate in physical and mathematical sciences, docent;
Yurkin I.M. – associate professor of the Department of Electronic Systems of Uzhhorod National University, a candidate in physical and mathematical sciences, docent;
Nebola I.I. – Head of the Department of Applied Physics and Quantum Electronics of Uzhhorod National University, a doctor of physical and mathematical sciences, professor;
Pop M.M. – associate professor of the Department of Applied Physics and Quantum Electronics of Uzhhorod National University, a candidate in physical and mathematical sciences, docent;
Rubish V.M. – Head of Uzhhorod Laboratory of Optoelectronics and Photonics Materials of the Institute for Information Recording of the National Academy of Science of Ukraine, doctor of physics and mathematics sciences, professor.

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О.О. Спесивих[1], Т.М. Заяць[1], І.М. Юркін[1], І.І.Небола[1], М.М. Поп[1,2], В.М. Рубіш[1,2]

Дослідження енергетичної структури кристалічних сполук в системах Ag(Tl)-As(P)-S(Se)

[1]*Ужгородський національний університет, Ужгород, Україна,*
[2]*Інститут проблем реєстрації інформації НАН України, Ужгород, Україна,* center.uzh@gmail.com

У роботі представлено результати дослідження особливостей формування валентної зони та зони провідності кристалічних сполук в системах Ag(Tl)-As(P)-S(Se) з sp^3-типом зв'язку методом фотоелектронної спектроскопії. Зі спектрального розподілу фотоемісії по енергіях визначено фотоелектронну роботу виходу $h\nu_0$ кристалів. Показано, що використання обмеженого базису (тільки потенціалів іонізації атомів та міжатомних відстаней) для кристалів з sp^3-типом зв'язку у рамках моделі ЛКАО дають достатньо точні результати положення верху валентної зони та величини електронної спорідненості. Розрахунки свідчать, що положення верху валентної зони визначають зв'язки атомів As-S(Se) і P-S(Se), тоді як гібридизовані орбіталі атомів Ag та Tl формуються у зоні провідності.

Ключові слова: поріг фотоемісії, напівемпіричні розрахунки, валентна зона, зона провідності, рівень Фермі, електронна спорідненість.