

UDC 544.723.2:661.8...5:544.662.3

EFFECT OF OXYGEN AND WATER ADSORPTION ON THERMOELECTRIC WORK FUNCTION FOR GeS SINGLE CRYSTALS

N.D. Savchenko ¹, T.N. Shchurova ¹, I.I. Opachko ¹, T.I. Panait ¹, K.O. Popovic ²

¹ Uzhgorod National University

13 Kapitulna Street, Uzhgorod 88000, Ukraine, shchrv@ukr.net

² NanoTecCenter Weiz Forschungsgesellschaft mbH

32 Franz-Pichler-Strasse, Weiz A-8160, Austria, karl.popovic@ntc-weiz.at

The results of theoretical and experimental studies of oxygen and water adsorption effect on thermoelectric work function for GeS single crystals are presented. Surface bending of the energy bands under oxygen and water molecules adsorption has been determined in terms of the theoretical approach developed by W.A. Harrison based on LCAO and pseudopotential methods. Calculated values of surface bending of the energy bands under oxygen and water adsorption for GeS single crystals are in quantitative agreement with experimental values for thermoelectric work function changes obtained from the measurements of contact potential difference.

INTRODUCTION

The steady interest to the investigation of A^{IV}B^{VI} narrow-band-gap semiconductors during last decades is due to the specific optoelectronic properties of these materials allowing their use in crystalline, glassy, colloidal nanostructure forms for optical data recording and storage, sensors, switching devices, etc. [1, 2]. In recent years intensive theoretical works on the effect of adsorption on the surface conductivity and work function for the semiconductor substrates are carried out (see, e.g., [3] and references therein). This interest is determined by the increased attention to the development of sensor electronic devices. The lack of experimental data for verification of different theoretical models is mentioned by many authors. Germanium sulphide attracts special attention being in the intermediate state between a true layered structure and a three-dimensional one [2]. The present work is intended to clarify the effect of ambient gases adsorption on the band gap structure for germanium sulphide layered single crystals.

COMPUTATION

The procedure of simulation of the energy bands and electronic states in the band gap was based on the combination of tight-binding and pseudopotential picture proposed by W.A. Harrison [4] and developed by us for binary chalcogenides [5, 6]. The energy values have been determined in the centre of the Brillouin zone. When constructing the energy

band diagrams, we used the atomic terms within Hartree-Fock approximation and intra-atomic Coulomb repulsion energies. The surface bending of the energy band was calculated as a difference between the energy of surface states before reconstruction and the Fermi level. Fermi level was determined with account of position of the levels formed by homopolar bonds, non-bonding and hybrid orbitals according to the procedure described in Ref. [7].

The energy positions of valence band maximum (E_v) and conduction band minimum (E_c) for GeS were determined using the universal tight-binding parameters from the expressions:

$$E_v = \frac{\varepsilon_p^{Ge} + \varepsilon_p^S}{2} - \sqrt{(V_2)^2 + (V_3)^2} + \Delta E_{s-o} + V_1 + \Delta E_{pd} + \frac{U}{2}, \quad (1)$$

$$E_c = \frac{\varepsilon_p^{Ge} + \varepsilon_p^S}{2} + \sqrt{(V_2)^2 + (V_3)^2} - V_1 + \frac{U}{2}, \quad (2)$$

where ΔE_{pd} is the upward shift of the valence band due to pd -coupling in terms of the lowest order perturbation theory:

$$\Delta E_{pd} = \frac{E_{pd}^2}{\varepsilon_p - \varepsilon_d}, \quad E_{pd} = \frac{10\sqrt{15}}{3\pi} \frac{\hbar^2}{md^4} \sqrt{r_p r_d^3}. \quad (3)$$

In these equations ε_s , ε_p , and ε_d are Hartree-Fock terms, r_p and r_d are p - and d -state radii [4, 8]; the metallic bond energy $V_1 = (\varepsilon_s - \varepsilon_p)/4$, covalent bond energy $V_2 = 2.96\hbar^2/md^2$ [9] and energy of polar bond $V_3 = (\varepsilon_p^{Ge} - \varepsilon_p^S)/2$; \hbar is Planck's constant divided by 2π , m is the electron mass, d is interatomic distance.

The values for the intra-atomic Coulomb repulsion energy, U , and spin-orbit splitting, ΔE_{s-o} , were determined as mean value for two components [10].

Changes in the Fermi level, E_F , and work function, $\Delta\Phi$, under adsorption of oxygen and water were calculated following the equations

$$E_F^{GeS} = \frac{1}{2} \left(E_{sp^3}^{Ge} + \frac{\varepsilon_p^{Ge} + \varepsilon_p^S}{2} \right), \quad E_{F^{O_2}} = \varepsilon_p^O + \left(\frac{U}{2} \right)^O,$$

$$E_F^{H_2O} = \frac{\varepsilon_s^H + \varepsilon_p^O}{2} + \left(\frac{U}{2} \right)^{H_2O}, \quad \Delta\Phi = |E_F^{GeS} - E_F^{O_2/H_2O}|. \quad (4)$$

In the simulation of surface electronic structure under adsorption of oxygen and water molecules we have accounted for the interatomic distances and different state types reported in [11, 12, etc].

EXPERIMENTAL

The starting GeS material was synthesized in sealed to 133 Pa silica ampoules by melting high-purity (5N) Ge and S components [13]. Germanium sulphide single crystals were grown by Bridgman-Stockbarger technique in vertical two-zone furnace at a temperature gradient in the growth zone of 3–5 K/mm and a pulling rate of 0.12–0.18 mm/h. The studies of the oxygen and water molecules adsorption effect on the crystal properties were conducted by means of the device providing specified pressure of adsorbing substances. Thermoelectric work function was determined from the measurements of the contact potential difference. Reference electrode was made of gold. All the measurements were conducted at 300 K.

RESULTS AND DISCUSSION

Calculated energy parameters for GeS single crystals and for O_2 and H_2O molecules are given in Table 1 and Table 2, respectively. Fig. 1 illustrates energy bands formation from Ge $4p$ and S $3p$ atomic terms via antibonding, σ^* , and bonding, σ , states for GeS with account of spin-orbit splitting and pd -coupling. Fermi level is fixed between Ge sp^3 hybrid and Ge $4p/S 3p$ levels. It is assumed that Fermi level for O_2 and H_2O molecules is formed by the shift of O $2p$ and H $1s/O 2p$ hybrid levels for the respective $U/2$ values (see, Table 1).

Table 1. Interatomic distance and energy parameters for GeS single crystals

	d , nm	V_1 , eV	V_2 , eV	V_3 , eV	$U/2$, eV	ΔE_{s-o} , eV	ΔE_{pd} , eV
GeS	0.286	2.53	2.77	2.14	4.24	0.06	0.08

Table 2. Interatomic distance, energy parameters, theoretic ($\Delta\Phi^{\text{theory}}$) and experimental ($\Delta\Phi^{\text{exp}}$) values of work function shift for oxygen and water molecules

	d , nm	V_2 , eV	V_3 , eV	$U/2$, eV	E_F , eV	$\Delta\Phi^{\text{theory}}$, eV	$\Delta\Phi^{\text{exp}}$, eV
O_2	0.120	6.77	–	7.23	9.54	0.16	0.12
H_2O	0.153	4.00	1.59	6.02	9.17	-0.21	-0.25

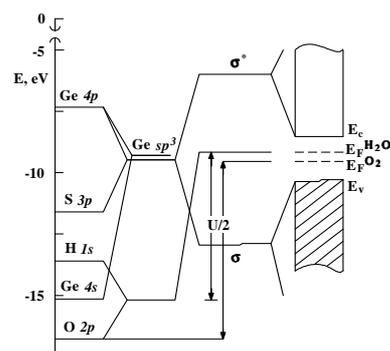


Fig. 1. Illustration of the energy bands formation from the atomic terms for GeS and Fermi level formation for O_2 and H_2O molecules

Fig. 2 shows electronic states in the band gap of GeS single crystals attributed to the intrinsic defects, possible band-to-band transitions, and Fermi level in GeS single crystal. Numbers in parentheses are given for the comparison of the calculated energy values with the experimental data on electroreflectance and photoluminescence in GeS single crystals presented in Ref. [14]. Close quantitative agreement of the calculated gap states with experimental data is seen.

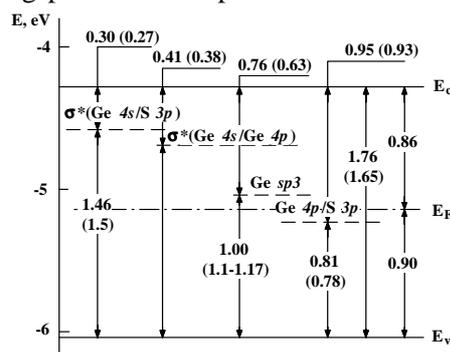


Fig. 2. Electronic levels, band-to-band transitions, Fermi level in GeS single crystal

Oxygen and water adsorption effect on the energy bands for the surface of GeS single crystal is shown in Fig. 3 *a, b*, respectively. Dotted lines correspond for the perfect GeS surface.

Calculated values for the electronic states of GeS and energy positions of the states attributed to oxygen and water molecules in the band gap suggest

that adsorption of the oxygen decreases the work function and thus, increases the conductivity, when water adsorption tend to increase the work function and to respective decrease in conductivity.

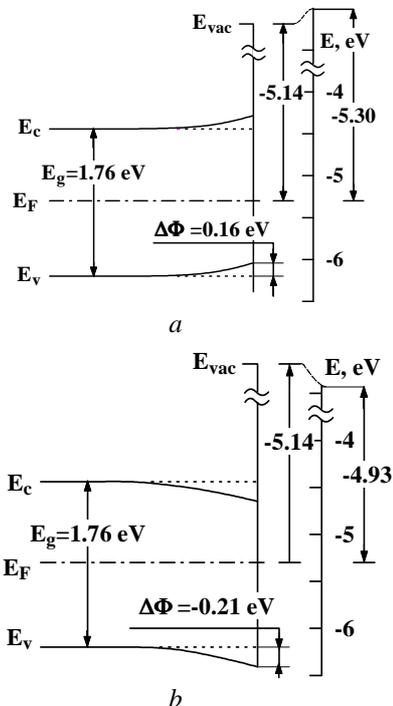


Fig. 3. Energy band diagram under oxygen (a) and water (b) adsorption for GeS surface

For the verification of theoretical results obtained within the proposed procedure we have conducted the experiments on oxygen and water adsorption effect on conductivity and thermoelectric work function for GeS single crystals. Similar behaviour for both dark current and work function under oxygen and water adsorption was observed. Opposite sign changes in thermoelectric work function with pressure under oxygen (curve 1) and water (curve 2) adsorption is shown in Fig. 4a for GeS single crystals. Work function increases with pressure up to $\sim 5 \cdot 10^3$ Pa and then is kept stable. Fig. 4b shows the kinetics of work function changes under oxygen (curve 1) and water adsorption at a pressure of $1.3 \cdot 10^3$ Pa (curve 2) for GeS single crystals.

It is assumed that the increase observed in conductivity and work function and their time dependences for the investigated single crystals under chemisorption of oxygen takes place via strong acceptor-type bonding. The decrease in conductivity and work function along with their kinetics under water adsorption indicate that its chemisorption takes place via strong donor-type bonding.

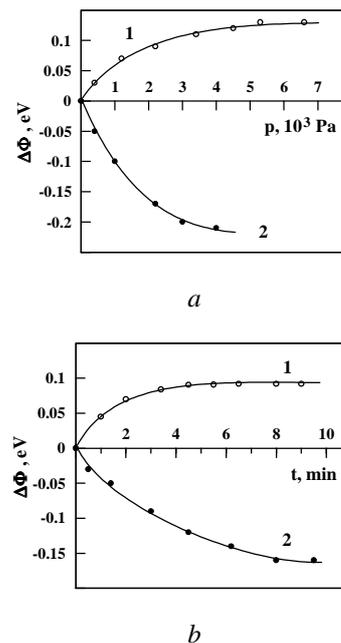


Fig. 4. Thermoelectric work function changes versus pressure (a) and versus time at a pressure of $1.3 \cdot 10^3$ Pa (b) for GeS single crystals under oxygen (curve 1) and water (curve 2) adsorption

CONCLUSIONS

Surface bending of the energy bands under oxygen and water adsorption has been calculated within modified theoretical approach developed by W.A. Harrison. The thermoelectric work function for GeS single crystals under oxygen and water adsorption has been measured by contact potential difference. Opposite sign effect of oxygen and water molecules adsorption on the surface bending of the energy bands and thermoelectric work function for GeS single crystals has been found. A quantitative agreement has been revealed between the calculated values of the surface bending of energy bands and the experimental work function values for GeS single crystals under oxygen and water molecules adsorption.

REFERENCES

1. Vaughn D.D., Patel R.J., Hickner M.A., Schaak R.E. Single-crystal colloidal nanosheets of GeS and GeSe // J. Am. Chem. Soc. – 2010. – V. 132, N 43. – P. 15170–15172.
2. Solanki G.K., Patel D.B., Unadkat S.R., Agarwal M.K. Synthesis and characterization of germanium monosulphide (GeS) single crystals grown using different transporting agents // Pramana (Journal of physics). – 2010. – V. 74, N 5. – P. 813–825.
3. An'chkov D.G., Davydov S.Yu. Effect of adsorption on the surface mobility of carriers in the

- semiconductor substrate // Phys. Solid State. – 2011. – V. 53, N 4. – P. 820–823.
- Harrison W.A. Elementary Electronic Structure, – London: World Scientific Publishing Co., 2004. – 838 p.
 - Shchurova T.N., Savchenko N.D., Kondrat A.B., Opachko I.I. Auger analysis and simulation of electronic states for Ge₃₃As₁₂Se₅₅ - p-Si heterojunction // Surf. Interface Anal. – 2006. – V. 38. – P. 448–451.
 - Shchurova T., Savchenko N., Kondrat A. et al. Simulation of the surface bending of energy band for binary chalcogenide semiconductors // Photoelectronics. – 2008. – V. 17. – P. 104–107.
 - Savchenko N.D., Shchurova T.N., Popovych K.O. et al. Simulation of electronic states in the band gap of ZnS: Cu, Cl crystallophosphors // Semiconductor Physics, Quantum Electronics & Optoelectronics. – 2004 – V. 7, N 2. – P. 133–137.
 - Mann J. B. Atomic Structure Calculations. I. Hartree-Fock Energy Results for Elements from Hydrogen to Lawrencium. – Springfield: Clearinghouse, 1967. – P. 22151–22160.
 - Harrison W.A. Coulomb interactions in semiconductors and insulators // Phys. Rev. B. – 1985. – V. 31. – P. 2121–2132.
 - Harrison W.A. Total energies in the tight-binding theory // Phys. Rev. B. – 1981. – V. 23. – P. 5230–5245.
 - Paxton A.T., Kohanoff J.J. A tight binding model for water // J. Chem. Phys. – 2011. – V. 134. – P. (044130) 1–11.
 - Morrill J.S., Ginter M.L., Hwang E.S. et al. Two-photon REMPI spectra from a¹Δ_g and b¹Σ_g⁺ to d¹Π_g in O₂ // J. Mol. Spectrosc. – 2003. – V. 219, N 2. – P. 200–216.
 - Bletska D.I., Madyar I.I., Mikulaninets S.V., Sichka M.Yu. Electrical and photoelectric properties of GeS layered crystals grown by different techniques // Inorg. Mater. – 2000. – V. 36, N 6. – P. 544–550.
 - Bletska D.I., Budiansky V.I., Gorodetsky I.Ya. et al. Investigation of local centres in layered GeS compound // Physics and Technology of Semiconductors. – 1975. – V. 9, N 8. – P. 1512–1516. (in Russian).

Received 31.05.2011, accepted 06.06.2011

Вплив адсорбції кисню і води на термоелектричну роботу виходу монокристалів GeS

М.Д. Савченко, Т.М. Щурова, І.І. Опачко, Т.І. Панайт, К.О. Попович

Ужгородський національний університет
вул. Капітульна 13, Ужгород 88000, Україна, shchrv@ukr.net
Науково-дослідне товариство НаноТехЦентр
вул. Франца Піхлера 32, Вайц А-8160, Австрія, karl.popovic@ntc-weiz.at

Представлено результати теоретичних та експериментальних досліджень впливу адсорбції молекул кисню та води на термоелектричну роботу виходу монокристалів GeS. Поверхневий вигин енергетичних зон при адсорбції кисню та води визначався в рамках теоретичного підходу, розробленого У.А. Харрісоном на основі методів ЛКАО та псевдопотенціалу. Розраховані значення поверхневого вигину енергетичних зон при адсорбції молекул кисню та води для монокристалів GeS кількісно узгоджуються з експериментальними значеннями зміни термоелектричної роботи виходу, одержаними з вимірів контактної різниці потенціалів.

Влияние адсорбции кислорода и воды на термоэлектрическую работу выхода монокристаллов GeS

Н.Д. Савченко, Т.Н. Щурова, И.И. Опачко, Т.И. Панайт, К.О. Попович

Ужгородский национальный университет
ул. Капитульная 13, Ужгород 88000, Украина, shchrv@ukr.net
Научно-исследовательское общество НаноТехЦентр
ул. Франца Пихлера 32, Вайц А-8160, Австрия, karl.popovic@ntc-weiz.at

Приведены результаты теоретических и экспериментальных исследований влияния адсорбции молекул кислорода и воды на термоэлектрическую работу выхода монокристаллов GeS. Поверхностный изгиб энергетических зон при адсорбции молекул кислорода и воды определялся в рамках теоретического подхода, разработанного У.А. Харрисоном на основе методов ЛКАО и псевдопотенциала. Рассчитанные величины поверхностного изгиба энергетических зон при адсорбции молекул кислорода и воды для монокристаллов GeS количественно согласовываются с экспериментальными значениями изменения термоэлектрической работы выхода, полученными из измерений контактной разности потенциалов.