Ab initio study of the piezoelectric effects of the 2D semiconductors of IV group monochalcogenides (GeSe, GeS)

Balabai R.M, Zadorozhnii V.M. *E-mail:balabai@i.ua*, vitaliy_zadorozhniy@ukr.net

Kryvyi Rih State Pedagogical University, 54 Gagarina Ave., Kryvyi Rih, 50086, Ukraine.

Introduction

The piezoelectric effect in nanostructured semiconductor attracts attentions in recent years. Since Zhong Lin Wang group observed piezoelectric generation in a ZnO nanowire and coined a new term in 2006, which is piezotronics [1]. The piezotronics takes advantage of the coupling properties of piezoelectric effect and semiconductor characteristic. The rapid development of piezoelectric applications, including wearable electronics and human–machine interfacing, put forward a new requirement for piezoelectric materials, which must be highly flexible and atomically thin. However, conventional piezoelectric materials, such as piezoelectric ceramics and piezoelectric semiconductors suffer from fragile and bulk characteristics; therefore, 2D materials with atomic layer thickness and mechanical flexibility have been regarded as a new generation of piezoelectric materials. Existing 2D materials are piezoelectric if they fulfill two criteria: they must have a non-symmetric crystal structure and they must be non-metallic [2]. The family of 2D semiconductors, group IV monochalcogenides is non piezoelectric in the bulk form as they are centro-symmetric. However, their inversion centers disappear in mono-layers, resulting in piezoelectricity [3]. The strong in-plane covalent bonding and weak interlayer van der Waals interaction in these 2D materials provides high in-plane stability allowing to produce it freestanding in nature. The study of piezoelectricity at the atomic level is fundamentally interesting.

In this paper the piezoelectric effects of the 2D semiconductors of IV group monochalcogenides (GeS, GeSe) are studied by methods of the density functional theory and first-principles pseudopotential based on own program code. The spatial distribution of valence electron density, density of states, and Coulomb potential along transverse direction are calculated. The redistribution of the valence electrons in films with an even number of mono-layers (centro-symmetric) and with an odd number (non centro-symmetric) under mechanical action are discussed.

Research methods and models

All calculations have been made with the proprietary source code [4]. The basic states of the electron-nucleus systems were detected by means of the self-consistent solution of Kohn-Sham one-particle equations:

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + \frac{\partial U}{\partial n(r)}\right\}\psi_i(r) = \varepsilon_i \psi_i(r) \qquad (1)$$

In the solution of these equations, the pseudopotential formalism was used, according to which a solid is considered as a set of valence electrons and the ion cores. In the pseudopotential approximation, the operator of the pseudopotential V_{PS}, which describes the interaction of valence electrons with the core, is small, and the corresponding pseudo-wavefunction is smooth. Bachelet-Hamann-Schlüter *ab initio* pseudopotential is used by us. The full crystalline potential is constructed as the sum of ion pseudopotentials that are not overlapping and associated with ions (nucleus + core electrons), located at the $\vec{R}_S$ positions that are periodically repeated for crystals:

$$V_{crystal}(\vec{r}) \rightarrow V_{PS}(\vec{r}) = \sum_{\vec{p}}\sum_{S}\hat{V}_S^{PS}(\vec{r}-\vec{p}-\vec{R}_S) \qquad (2)$$

For nonperiodic systems, such as a thin film or a cluster the problem of lack of periodicity is circumvented by use of the supercell method. Namely, the cluster is periodically repeated but the distance between each cluster and its periodic images is so large that their interaction is negligible. The ubiquitous periodicity of the crystal (or artificial) lattice produces a periodic potential and thus imposes the same periodicity on the density (implying Bloch's Theorem). The Kohn-Sham potential of a periodic system exhibits the same periodicity as the direct lattice and the Kohn-Sham orbitals can be written in Bloch form:

$$\psi(\vec{r}) = \psi_i(\vec{r},\vec{k}) = exp(i\vec{k}\cdot\vec{r})u_i(\vec{r},\vec{k}) \qquad (3)$$

where $\vec{k}$ is a vector in the first Brillouin zone. The functions $u_i(\vec{r},\vec{k})$ have the periodicity of the direct lattice. The index «i» runs over all states. The periodic functions $u_i(\vec{r},\vec{k})$ are expanded in the plane wave basis. This heavily suggests using plane waves as the generic basis set in order to expand the periodic part of the orbitals. Since plane waves form a complete and orthonormal set of functions, they can be used to expand orbitals according to:

$$\Psi_j(\vec{k},\vec{r}) = \frac{1}{\sqrt{N_0\Omega}}\sum_{\vec{G}}b_j(\vec{k}+\vec{G})\,exp(i(\vec{k}+\vec{G})\vec{r}) \qquad (4)$$

where $\vec{G}$ is the vector in the reciprocal space, Ω is the volume of the elemental cells which consists of a periodic crystal or an artificial superlattice when reproducing nonperiodic objects. The equation (1) after the Fourier transform to the reciprocal space has the form:

$$\sum_{\vec{G}}\left[\left\{\frac{\hbar^2}{2m}(\vec{k}+\vec{G})^2 - \varepsilon_j\right\}\delta_{\vec{G},\vec{G}'} + V_{KS}(\vec{k}+\vec{G},\vec{k}+\vec{G}')\right]b_j(\vec{k}+\vec{G}) = 0 \qquad (5)$$

where V_{KS} is the Kohn-Sham potential:

$$V_{KS}(\vec{k}+\vec{G},\vec{k}+\vec{G}') = V_{ps}(\vec{k}+\vec{G},\vec{k}+\vec{G}') + V_H(\vec{G}'-\vec{G}) + V_{XC}(\vec{G}'-\vec{G}) \qquad (6)$$

where V_{xc} is the exchange and correlation potential. To calculate its we used Ceperley-Alder's approximation that has been parameterized by Perdew and Zunger. The main value in the formalism of the functional of the electron density is the charge density. It is estimated from a self-consistent solution of equations (1) which should be performed at all points of the non-reduced section of the Brillouin zone:

$$\rho(G) = \frac{2}{N_T}\sum_k\sum_j\sum_{\alpha\in T}\sum_{G'}b_j^*(k+G'+\alpha G)b_j(k+G') \qquad (7)$$

where the index j runs over all occupied states, $\vec{k}$ is a vector in the first Brillouin zone, N_T is the number of the operators α in the point group T of the atomic basis and the factor 2 takes into account the spin degeneracy.

Estimated effort can be reduced if there is the integral over the Brillouin zone to approximate by summing over a special points of the Brillouin zone. It is possible to replace with satisfactory precision the summation by the finite number of special points to one point in the Brillouin zone. It is possible to restrict only the Γ-point in the Brillouin zone, especially as it relates to the artificial periodic systems.

Distribution of electrons along the energy zones for Γ-state of the investigated structures was found by means of numerical calculation of derivative $\lim_{\Delta E\rightarrow 0}\Delta N/\Delta E$ where ΔN is a number of the allowed states for the ΔE interval of energy. The one-particle energy spectrum was obtained from calculation of the eigenvalues of the Kohn-Sham matrix. In accordance with ideology of the electronic density functional, the occupied states at absolute zero temperature were defined. It allowed to define position of the last occupied state, their number being half the number of electrons (due to ignoring the spin of the electron), and position of the first free states.

Coulomb potential along the given direction was calculated by the formula that in the reciprocal space has the form:

$$V_h(G) = \frac{4\pi e^2\rho(G)}{G^2} \qquad (8)$$

where $\rho(G)$ is the Fourier component of the electron density (7).

Our calculations were made under the following conditions: the Brillouin zone (ZB) summation was changed by calculation at one point of the ZB (Γ-point). The self-consistency iterations were terminated if the results of the current iteration calculation coincided with the previous one with a predetermined error. Their number varied depending on the object being calculated, but usually, our results coincided after 5-6 iterations. The number of plane waves in the expansion of the wave function was truncated by trial calculations and evaluation of the physicality of the obtained results (spatial distribution of electron density, the magnitude of the gap in the energy electron spectrum between the last occupied state, and the first unoccupied, general ideas about the simulated nanostructure) or evaluation of the obtained results in comparison with the results obtained by other authors. Often the number of plane waves was chosen to be about 20-25 waves per base atom. The atomic basis was not optimized.

To estimate the redistribution of the electron charge between atoms, the expression in the neighborhood of an atom α was calculated in the volume V:

$$q_\alpha = Z_\alpha - \int_{V_\alpha}n(r)d^3r \qquad (9)$$

In the studied atomic systems, the artificial translational symmetry was introduced by constructing of a super-lattice with a primitive tetragonal cell and the atomic basis which contains the complete information about the studied system. The cell was translated in three orthogonal directions. For calculations such objects were reproduced:

Object 1: the infinite free-standing film with two mono-layers (bi-layer) (centro-symmetric) of GeS. The GeS bulk has an orthorhombic structure with eight atoms per primitive unit cell, four of each species, in the coordinate positions $\pm\left(u,\frac{1}{4},\omega\right);\pm\left(\frac{1}{2}-u,\frac{1}{4},\frac{1}{2}+\omega\right)$ [5]. The primitive unit cell contains two puckered layers, stacked on top of each other. The bilayer is obtained by increasing the lattice supercell vector perpendicular to the plane of the layers. The monolayer has four atoms per unit cell. Each atomic species is covalently bonded to three neighbors of the other atomic species, forming zigzag rows of alternating elements. Thus, there is in each atom a lone pair pushing its three bonds towards a tetrahedral coordination, just like in black phosphorus, resulting in its characteristic waved structure. The lattice parameters and fractional atomic positions are u(Ge)= 0.127a, w(Ge)= 0.122c, u(S)= 0.499a, w(S)= -0.151c, a=4.30 Å, b=3.64 Å, c=10.47 Å. The single cell of the super-lattice was with parameters

a=4.30 Å, b=3.64 Å, c=12.17 Å; the base consisted of 8 atoms (four of Ge atoms and four of S atoms), as in Fig. 1 (left).

Object 2: the infinite free-standing film with one mono-layer (non centro-symmetric) of GeS. The single cell of the super-lattice (a=4.30 Å, b=3.64 Å, c=18.52 Å) contains two mono-layers that are distant and do not interact with each other.

Object 3: the infinite free-standing film with two mono-layers (bi-layer) (centro-symmetric) of GeSe. The GeSe bulk has an orthorhombic structure with eight atoms per primitive unit cell, four of each species, in the coordinate positions $\pm\left(u,\frac{1}{4},\omega\right);\pm\left(\frac{1}{2}-u,\frac{1}{4},\frac{1}{2}+\omega\right)$ [5]. The lattice parameters and fractional atomic positions are u(Ge) = 0.127a, w(Ge) = 0.122c, u(Se) = 0.499a, w(Se) = -0.151c, a=4.30 Å, b=3.64 Å, c=10.47 Å. The single cell of the super-lattice was with parameters a=4.388 Å, b=3.833 Å, c=12.7 Å.

Object 4: the infinite free-standing film with one mono-layer (non centro-symmetric) of GeSe. The single cell of the super-lattice (a=4.388 Å, b=3.833 Å, c=18.52 Å) contains two mono-layers that are distant and do not interact with each other, as in Fig. 1 (left).

Modeling of mechanical effects of the static compression type was carried out by changing the corresponding coordinates of atoms in the direction of the compression force: for a film with free surfaces (001), the compression force acted in the [001] direction, which is conjugate to the Cartesian direction Z, and, accordingly, Z-coordinates of atoms decreased up to 9% of the original with a step of 1%.
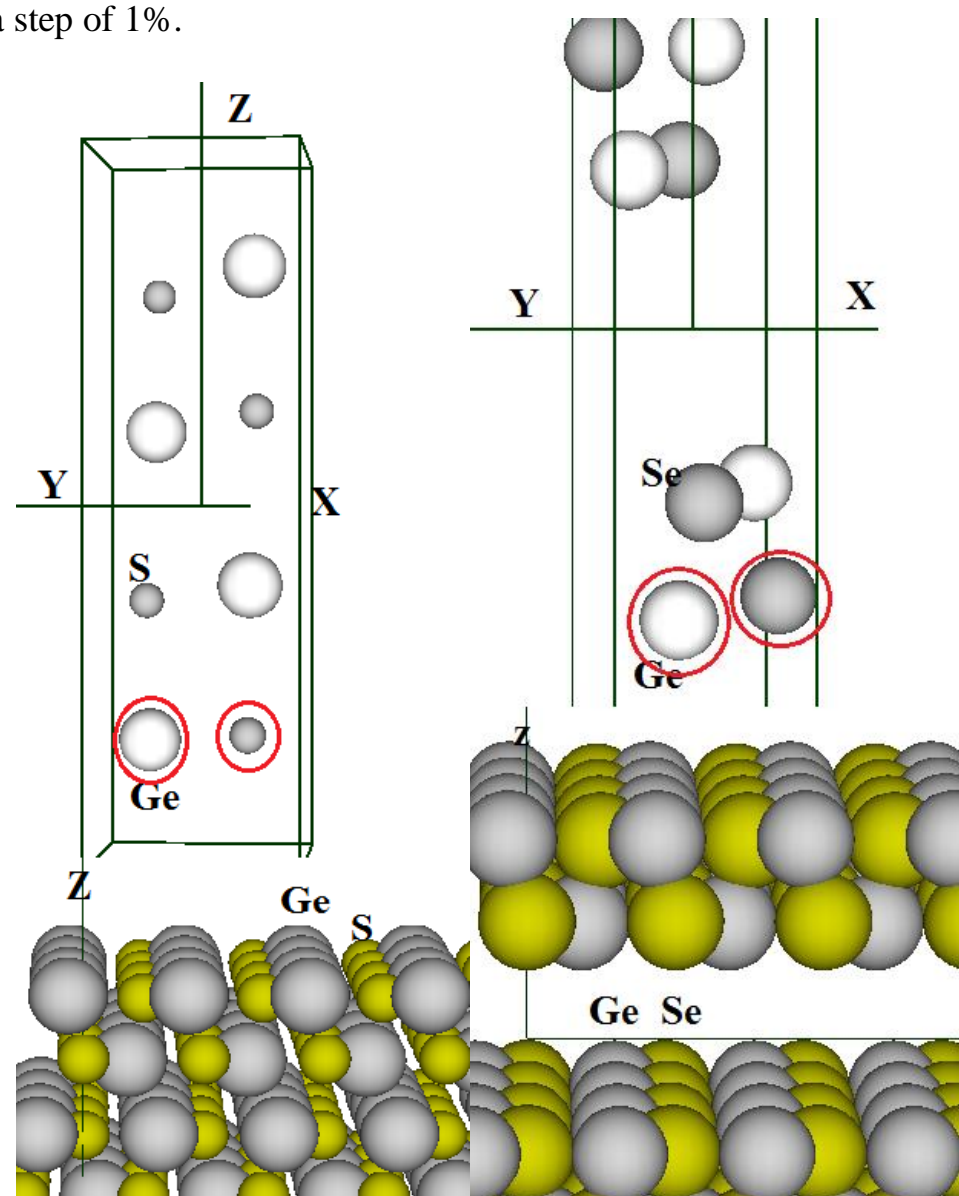

Fig. 1. The single cells of an artificial super-lattices with atomic bases for different objects of computation: object 1, one the infinite free-standing film with two mono-layers (bi-layer) (centro-symmetric) of GeS (left); object 3, two the infinite free-standing film with one mono-layer (non centro-symmetric) of GeSe (right).

Result and discussion

Analyzing changes in the distribution of valence electrons in the area of the films with an even and odd number of mono-layers, we evaluated the degree of influence of internal mechanical stress and the presence of a center of symmetry in the atomic structure of the films on the value of the film's internal electric potential.

The results of the calculations are shown in tables 1, 2 and Fig. 2 - 3. Table 1 shows the values of electric charges on the cores of Ge, S, and Se atoms of objects 1–4, which are estimated according to formula (9) in a spherical volume with a radius of 1.3 Å (the atoms for which the charge was calculated were highlighted in Fig. 1 by circles) depending on the level of vertical compression of the films. Electric charges were calculated in the atomic system of units, in which the charge of an electron is equal to one.

Table 1.

Values of electric charges around the cores of surface Ge, S, Se atoms of objects 1–4 depending on film compression from 0% to 9%

| Atom	Object 1, GeS, bi-layer	Object 2, GeS, mono-layer	Object 3, GeSe, bi-layer	Object 4, GeSe, mono-layer
Ge	3,0145	1,4087	1,0414	2,9757
	2,9845	1,4096	1,0136	2,8503
	2,9438	1,5255	0,9837	2,4302
	2,8777	1,5086	0,9516	2,1960
	2,8375	1,4919	0,9178	1,5933
	2,8047	1,4782	0,8827	1,1707
	2,7927	1,4681	1,3035	1,0977
	2,7742	1,4601	1,3874	0,7955
	2,7389	1,4523	1,3604	0,5049
	2,6800	1,4381	1,3235	0,2841
S (Se)	-1,4000	-2,3170	-1,5072	3,7593
	-1,2078	-2,2674	-1,5048	3,483
	-1,0119	-1,8812	-1,5001	2,1069
	-0,4443	-1,8138	-1,4931	1,455
	0,1103	-1,7585	-1,4835	0,4487
	0,2247	-1,7021	-1,4716	0,0678
	0,3047	-1,6391	-1,2786	0,1918
	0,3424	-1,5696	-1,3268	0,0054
	0,3637	-1,4973	-1,3029	-0,1893
	0,3340	-1,4286	-1,2818	-0,3159
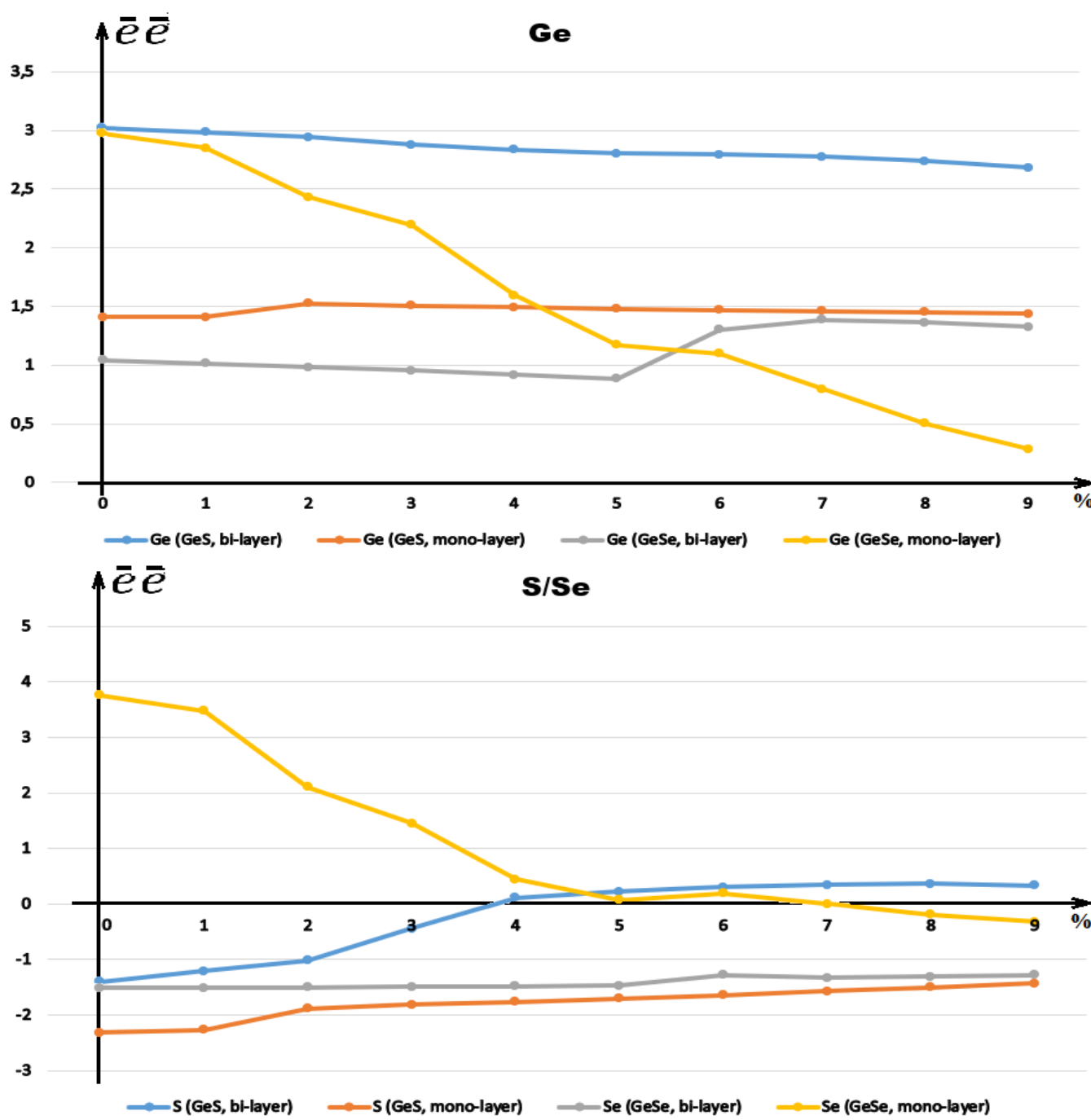
Fig. 2. The value of electric charges on atomic Ge, S and Se cores of objects 1–4 depending on film compression from 0% to 9%

Charge redistribution during compression between Ge atoms and S (or Se) atoms in GeS and GeSe bi-layers is more significant than in mono-layers. On the other hand, the charge redistribution during compression between Ge atoms and S atoms in mono-layer and bi-layer GeS is more significant than in mono-layer and bi-layer GeSe. The latter is connected with some difference in the electronegativity of Se and S atoms. Electronegativity of these elements according to the Pauling scale: Ge=2,0, S=2,6, Se=2,5, their atomic radii are as follows: Ge=1,3 Å, S=0,8 Å, Se= 1,4 Å. When the electronegativities of two atoms differ, the atom with a higher electronegativity exerts an electrostatic influence on the environment, as a result of which the electron shells shift in the other atom, i.e., a greater polarization of the Ge-S pair bond than the Ge-Se pair occurs. The share of ionicity of a covalent bond is caused by the appearance of an effective charge in polarized covalent pairs (see Table 1 and Fig. 2).

As for the spatial distributions of the valence electron density for the films shown in Fig. 3, they confirm a more significant rearrangement of the electron density during compression in bi-layer films of both GeS and GeSe, but more significant in GeS films.
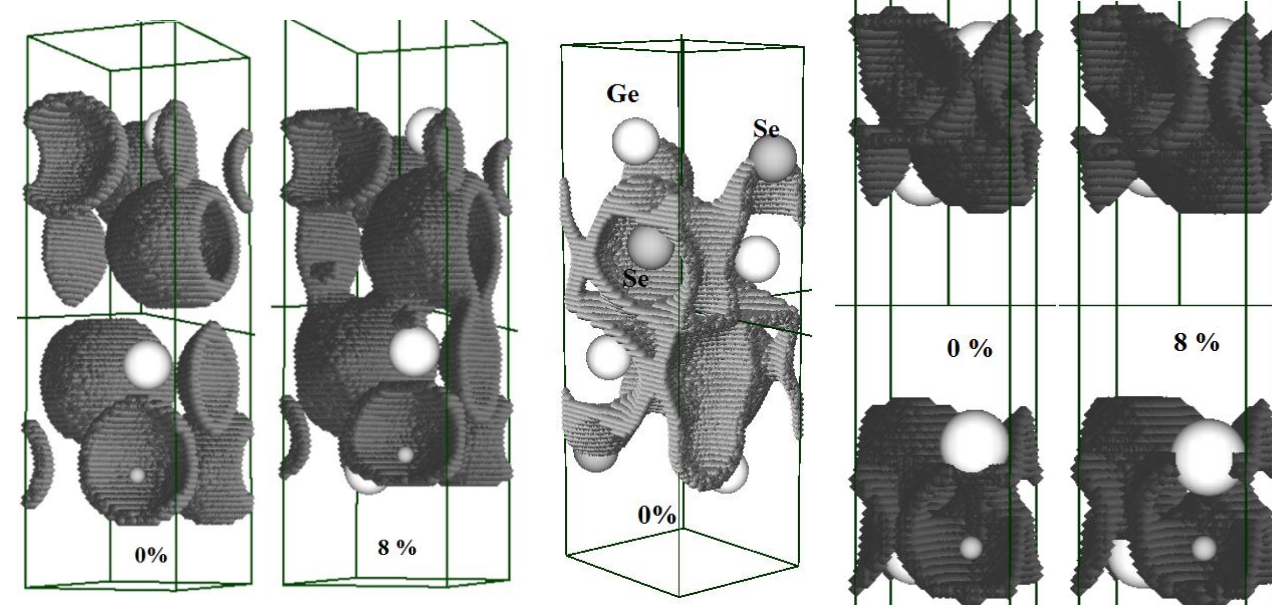

Fig. 3. Spatial distribution of valence electrons density within the interval of 0.2-0.1 of the maximum value in the GeS film (bi-layer, objects 1 - left), in the GeSe film (bi-layer, objects 1 - in the middle), in the GeS film (mono-layer, objects 2 - right)

Therefore, the vertical compression of the films leads to the redistribution of the charge, which causes the rearrangement of the internal electric fields with potentials across the films, the distribution form and values of which are given in Table 2 and Fig. 4.

Table 2.

The maximum values in the distribution of potentials of transverse electric fields in objects 1-4 depending on the compression of the films from 0% to 9%

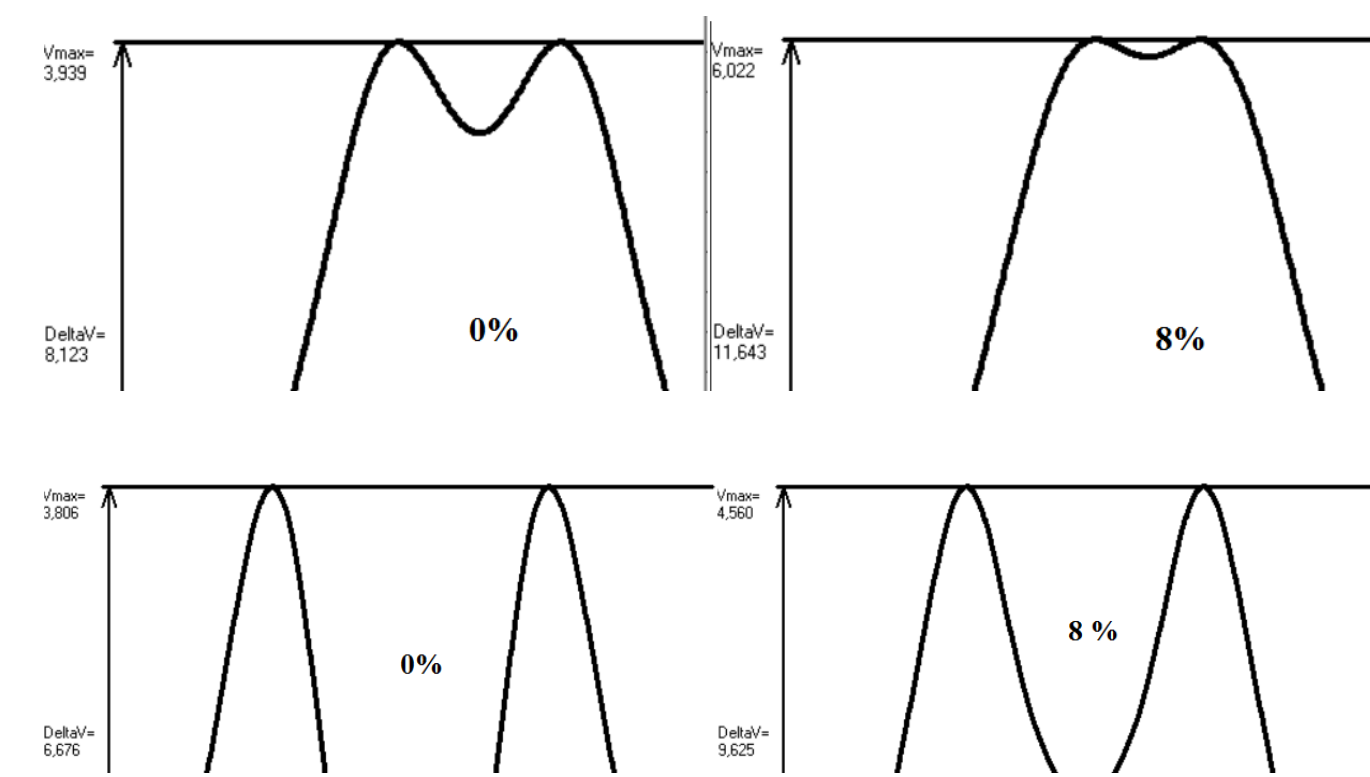| Object 1, GeS, bi-layer	Object 2, GeS, mono-layer	Object 3, GeSe, bi-layer	Object 4, GeSe, mono-layer
3,939	3,806	2,256	4,832
4,14	3,856	2,343	4,819
4,332	4,032	2,435	4,525
4,73	4,109	2,531	4,434
5,263	4,186	2,63	4,217
5,473	4,267	2,734	4,175
5,677	4,356	3,059	4,254
5,855	4,454	3,173	4,26
6,022	4,56	3,295	4,272
6,134	4,673	3,415	4,302

Fig. 4. Distributions of Coulomb potentials across (Z direction) a GeS film (bi-layer, object 1 - top) and a GeS film (mono-layer, object 2 - bottom)

The reliefs of the distribution of the Coulomb potential across the film consisting of two monolayers (bi-layer), which interact with each other by weak van der Waals forces and have strong covalent-ionic interactions within the monolayers, reflect the indicated interactions in their shape (Fig. 4, top). The compression of the bi-layer of the film makes the relief of the distribution of the Coulomb potential sharply in the direction from the region between the mono-layers to the outer side of the film. At the same time, the "working" potential difference is formed, precisely, on one mono-layer, but under the condition that it is a constituent part of the bi-layer, that is, in an atomic system that has a center of symmetry. Whereas on isolated mono-layers that do not have an inversion center, a potential is formed, and its distribution does not lead to a non-zero potential difference across the film (Fig. 4, bottom). This our conclusion clarifies the condition for the selection of 2D materials used in piezoelectricity.

Conclusion

The valence electron density spatial distribution, the densities of electron states, the widths of band gaps, the charges on surface's atoms, the Coulomb potentials for films with an even number of mono-layers (centro-symmetric) and with an odd number (non centro-symmetric) under mechanical action were calculated in the framework of the density functional and *ab initio* pseudopotential theories.

A significant rearrangement of the electron density is observed during compression of both GeS and GeSe bi-layer films than mono-layer films, but more significant in GeS films.

The reliefs of the distribution of the Coulomb potential across the film consisting of two monolayers (bi-layer), which interact with each other by weak van der Waals forces and have strong covalent-ionic interactions within the monolayers, reflect the indicated interactions in their shape. The compression of the bi-layer of the film makes the relief of the distribution of the Coulomb potential steeper in the direction from the region between the mono-layers to the outer side of the film. At the same time, the "working" potential difference is formed, precisely, on one mono-layer, but under the condition that it is a constituent part of the bi-layer, that is, in an atomic system that has a center of symmetry. Whereas on isolated mono-layers that do not have an inversion center, a potential is formed, and its distribution does not lead to a non-zero potential difference across the film.

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