Energy Band Gap tuning in Te doped WS₂/WSe₂ Heterostructures

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ABSTRACT

Understanding the possibility of band gap engineering in multilayers composed of two-dimensional materials is extremely important for modeling and creation of novel electronic and photonic devices. Stacking of WS₂ and WSe₂ monolayers looks especially attractive for applications due to direct gap of resulting heterostructure, especially taking into account the indirect-gap nature of their bulk state counterparts. We performed theoretical investigation of chalcogen atoms replacement in WS₂/WSe₂ heterostructure by isovalent Te atoms in order to reveal its effects on the band gap, electronic structure and density of states. The doped heterostructures were found to preserve semiconductor properties, whereas the gap changed its nature from direct to indirect in dependence of the position and the distance between substituting Te atoms. Te atoms in the S atom positions led preferably to an indirect gap and increased its value as compared to the pristine material; upon substitution of Se atoms the direct gap of the heterostructure is preserved but with a small reduction, whereas the substitution of both S and Se atoms changed the gap in a different way depending on Te position. This information makes possible the creation of multilayered structures with tunable gap important for novel generation of electronic and photonic devices.

KEYWORDS

TMD, heterostructure, tungsten diselenide, tungsten disulfide, hybrid crystal

INTRODUCTION

The discovery and experimental exfoliation of graphene [1] has led to an explosion of interest to many two-dimensional materials [2] like transition metal dichalcogenides (2D TMDs), where layers are bonded by van der Waals forces. It is known that monolayers of indirect-gap TMDs may become direct-gap semiconductors [3]. This fact, together with expectation of new electronic, optical, and catalytic properties [3-6], as well as great enhancement of photoluminescence quantum yield in going from the indirect-gap bulk crystal to the direct-gap monolayer [2], explains the interest to such class of materials. 2D TMDs attract much attention both in the form of freestanding films and heterostructures [7-8]. Monolayer WS_2 and WSe_2 were previously described as a direct-gap semiconductors with an experimental band gap of about 2.05-2.14 eV [9-10] and 1.65 eV, respectively [10]. This data are referring to optical bandgaps at room temperature without considering quasiparticle (e.g., excitons) effects. Presented in [10] theoretical gap values are 1.94 eV for WS_2, 1.74 eV for WSe_2 and 1.14 eV for WTe_2 monolayers; in our previous calculations we obtained 1.97 eV(WS_2) and 1.66 eV (WSe_2) [11]. Combining the layers of different TMDs will permit to obtain a hybrid crystal with a tunable gap. This fact was already shown in [8] and [12]. Authors [8] considered WS_2/WSe_2 and MoS_2/WSe_2 bilayers for two types of layer stacking and found a possibility to generate direct band gap bi-layers with the gap ranging from 0.79 eV to 1.157 eV. In [12] we examined two types of stacking for four different heterostructures ($MoS_2/MoSe_2$, MoS_2/WS_2, WS_2/WSe_2, $MoSe_2/WSe_2$) and in this paper we focused our attention on the WS_2/WSe_2 heterostructure, because it was the only one among four combinations which possessed a direct gap for two different arrangements of monolayers even after impurity and vacancies introduction. It is however worth noting that point defects (like vacancies or antisites) in monolayer TMDs, as well as different layer arrangement and orientation, may have significant impact on the gap value and nature [13-17]. For instance, the substitution by isovalent chalcogen atoms may change the band gap values and related characteristics of heterostructure that looks very promising for manipulation of its properties. We already considered the case when tellurium atom substituted the atoms of tungsten [18]. As far as such structure implies using of different materials prepared in separated technological process steps, each layer may possess different Te concentration. So, the present work focuses mainly on thoroughly determination of the impact of Te isovalent atoms substituting the chalcogen ones on electronic properties of WS_2/WSe_2 heterostructure in dependence on the positions and the distance between the substituting atoms.

THEORETICAL STUDY

The heterostructure considered was composed of one WS_2 layer and one WSe_2 layer, where one or more chalcogen (S or Se) atoms were substituted by Te ones in a different way. The distances between Te atoms varied from about 3.26 to 6.54 Å when substituting atom was only in one layer, and from 3.56 to

6.52 Å, when Te atoms were in both layers. 2H pristine phase was considered as the most stable polymorphic modification for this class of hexagonal layered 2D-materials with the space group P63/*mmc* [19]. The calculations within density functional theory were performed using PAW-LDA approximation realized in the VASP code [20] taking into account van der Waals forces acting between the monolayers by means of correction, described by J. Klimeš [21] as optB86b-vdW optimized exchange functional. The arrangement of the atoms corresponded to the hexagonal structure. A 2×2 translational cell with the vacuum layer between the heterostructures of about 15 Å was used. The atomic positions relaxed until forces acting on atoms were less than 0.01 eV/Å. We used the energy cutoff of 380 eV and the 9×9×2 grid of for Γ-centered mesh of k-points. The arrangement of the layers in heterostructure corresponded to crystal stacking found in the bulk material, i.e. chalcogen atoms of one layer sit on top of the metal atoms of the other layer. Doping effect in WS_2/WSe_2 heterostructure was achieved by replacing either one or two host chalcogen atoms in the system.

RESULTS AND DISCUSSION

First we modelled the WS_2/WSe_2 heterostructure within the scheme which was previously described in [12]. Then, we have considered three different ways of chalcogen atoms substitution: 1) Te atoms were located in WS_2 layer substituting S atoms; 2) Te atoms were located in WSe_2 layer substituting Se atoms; 3) Te atoms were located in both layers substituting S and Se atoms. As each monolayer is composed of a layer of tungsten atoms surrounded from the top and bottom by single layers of chalcogen atoms, Te atoms were placed either in top or bottom single layer, or in both of them. The bond lengths obtained in the doped structures are presented in **Table 1**. Comparison of these values with the bond lengths in defect-free structure, which are 2.43 Å (W-S) and 2.53 Å (W-Se), shows that impurity does not change greatly the lengths of this type of bonds, increasing mostly the bond length nearest to the substituting atom.

Table 1 Bond lengths (Å) in Te-doped WS_2/WSe_2 heterostructure

Bond length, Å	Te in WS_2 layer	Te in WSe_2 layer	Te in WS_2 and WSe_2 layers
S-Te	3.27-3.31	–	3.29-3.30
Se-Te	–	3.25-3.27	3.27-3.29
W-Te	2.70-2.73	2.70-2.71	2.71-2.73
W-S	2.43	2.43-2.44	2.42-2.43
W-Se	2.53-2.54	2.53-2.54	2.53-2.54

The electronic band spectra of pristine WS_2/WSe_2 heterostructure together with its side view are presented in Fig. 1. It is worth to note that the combination of two different materials, each of them is direct-gap only in its monolayer form, gives a direct-gap semiconductor with the first direct transition of 0.95 eV occurring at the K point.
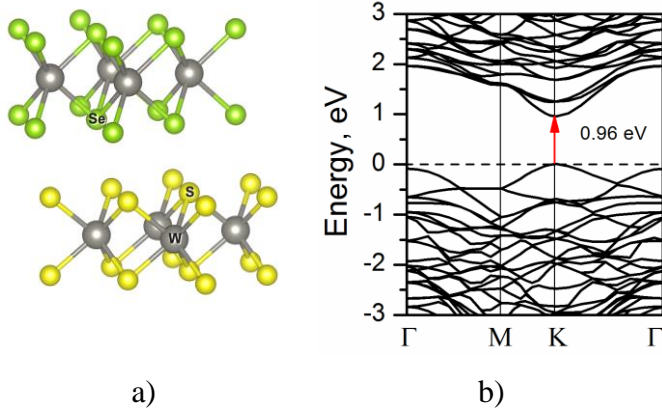
Figure 1 Side view (a) and electronic energy band diagram (b) of pristine WS_2/WSe_2 heterostructure. Zero on the energy scale corresponds to the top of the valence band

a)   b)

In order to evaluate the possibility of doping the system considered we calculated the corresponding formation energy in the presence of the defect. For a substitutional dopant the formation energy was defined as

$$E_f (Te) = E_{tot}(WS_2/WSe_2:Te) - E_{tot}(WS_2/WSe_2) + \mu_{host} - \mu_{Te}, \tag{1}$$

where $E_{tot}(WS_2/WSe_2:Te)$ is the total energy of the system with a substituted atom, $E_{tot}(WS_2/WSe_2)$ is the total energy of pristine structure, μ_{host} and μ_{Te} denote the chemical potentials of host chalcogen atoms (S or Se) and substituting Te atom, respectively, which are calculated from the respective bulk phases. In the case of S atom substitution we obtained E_f of about 1.2 eV and for Te in the site of Se atom E_f of about 0.9 eV, which is more energetically favorable. The formation energy in the latter case is lower as a radius of substitutional atom gets bigger and the size difference between the dopant and the chalcogen atom is less significant.

The band spectra of doped heterostructure with corresponding side views, showing the position of Te atoms in each case, are presented in Figs. 2-4. For all the band structures computed the conduction band minimum is located in the K point, whereas the valence band maximum is located either in the Γ or K points. Upon replacement of S atoms by Te ones the structure becomes preferably an indirect-gap semiconductor with the energy gap increasing up to 1.23 eV (Fig. 2). The single exception is the variant when one Te atom is located in the bottom S layer; this case is characterized by a direct gap with E_g of 0.97 eV. The increase of the gap instead of expected decrease due to lattice enlargement connected with the shift of valence band maximum from the K to Γ point and conduction band minimum to higher energies if compare with pristine structure. In contrary, when one or two Se atoms are replaced, all the

structures remain direct-gap semiconductors, and the band gap values decrease as compared to the pristine material (Fig. 3).
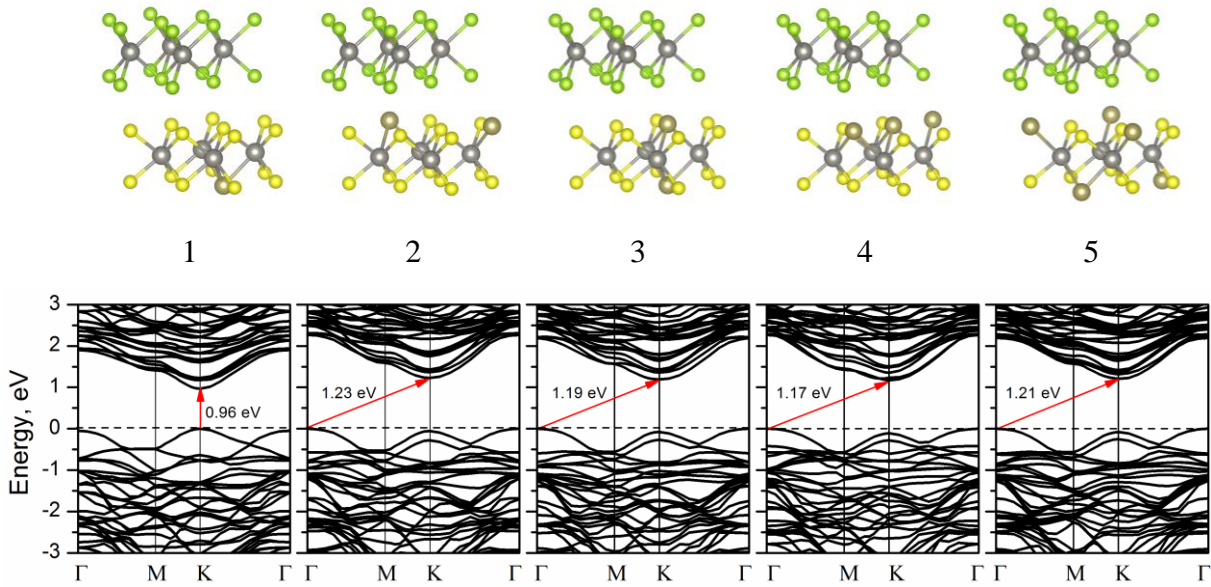
Figure 2 Side view (top) and electronic energy band diagram (bottom) of WS_2/WSe_2:Te heterostructure, Te atoms are in the S sites. Zero on the energy scale corresponds to the top of the valence band
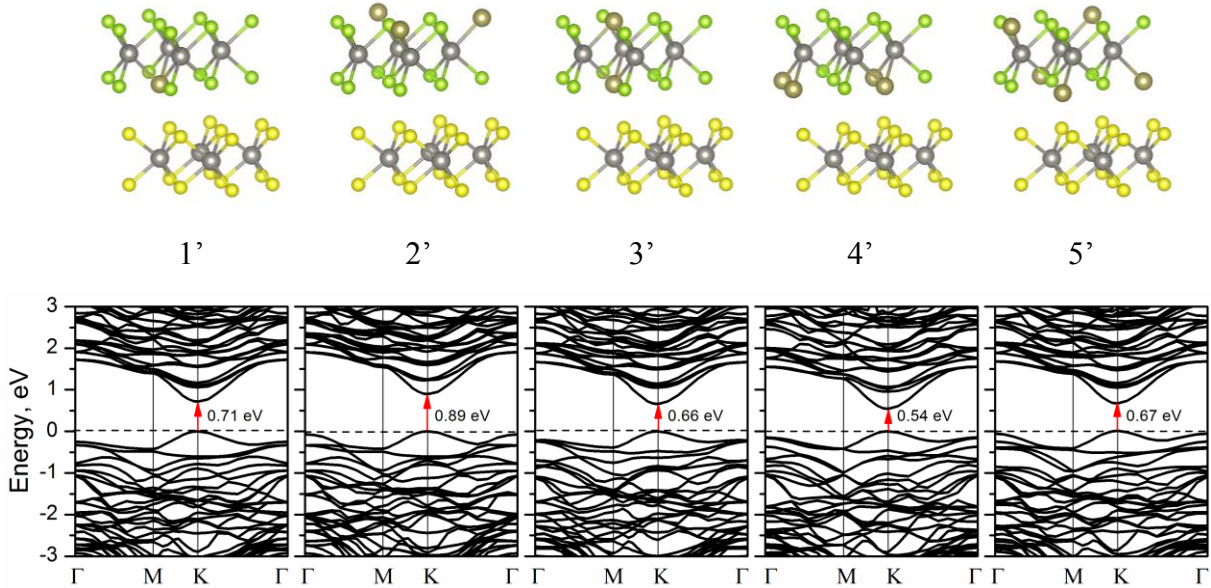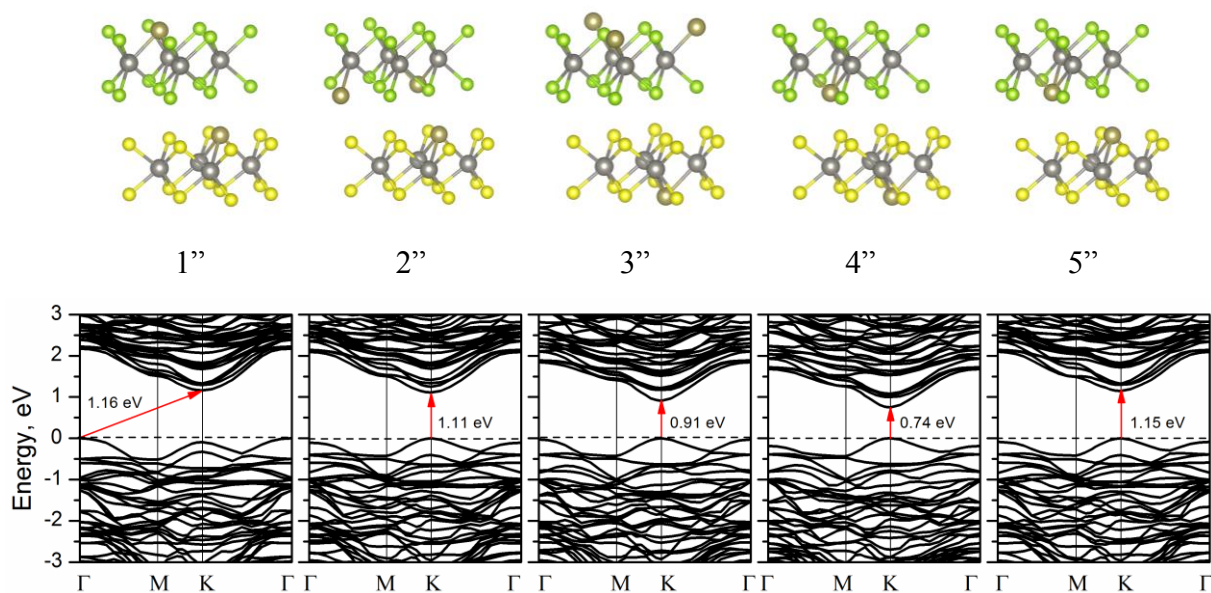

Figure 3 Side view (top) and electronic energy band diagram (bottom) of WS_2/WSe_2:Te heterostructure, Te atoms are in the Se sites. Zero on the energy scale corresponds to the top of the valence band

When one Te atom is located in WS_2 layer and another one is in WSe_2 layer, the indirect nature of the main gap occurs only in one case, when the distance between substituting atoms is maximal and is equal

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to 6.52 Å (Fig. 4). All the rest cases are characterized by the direct gaps. The band gaps are changing in a different way and may both increase or decrease as compared to the value for the pristine material depending on the position of substitutional atom. Such various gap changes can be explained by lattice distortion, which occurs upon impurity introduction. Te atom has a bigger radius in comparison with substituted ones, so the bond length becomes larger, leading to an extension of the lattice, and as a rule, decrease of the gap. However, as Te atoms break the symmetry within the layer of chalcogen atoms, the lattice becomes disproportional to some extent. As the radius of Te atom is closer to radius of Se, the deviation of the bond length from its equilibrium position is smaller and the gap changes are not so radical. In its turn, the difference between Te and S atoms radii is larger and the impurity atom enlarge lattice parameter in its proximity up to 3.28 Å, whereas it is diminishes up to 3.23 Å in another region, as compared to 3.26 Å lattice parameter of the material without Te substitution. As a consequence, the gap change in this case is more complicated and the shift of the valence band maxima from the K to Γ point occurs in that case together with the increase of the gap value. When impurity is located both in the S and Se sites the lattice is distorted to a different extent in each layer so the total effect of impurity is mixed and depends strongly on the mutual arrangement of impurity atoms.

Figure 4 Side view (top) and electronic energy band diagram (bottom) of WS_2/WSe_2:Te heterostructure, Te atoms are in S and Se sites. Zero on the energy scale corresponds to the top of the valence band

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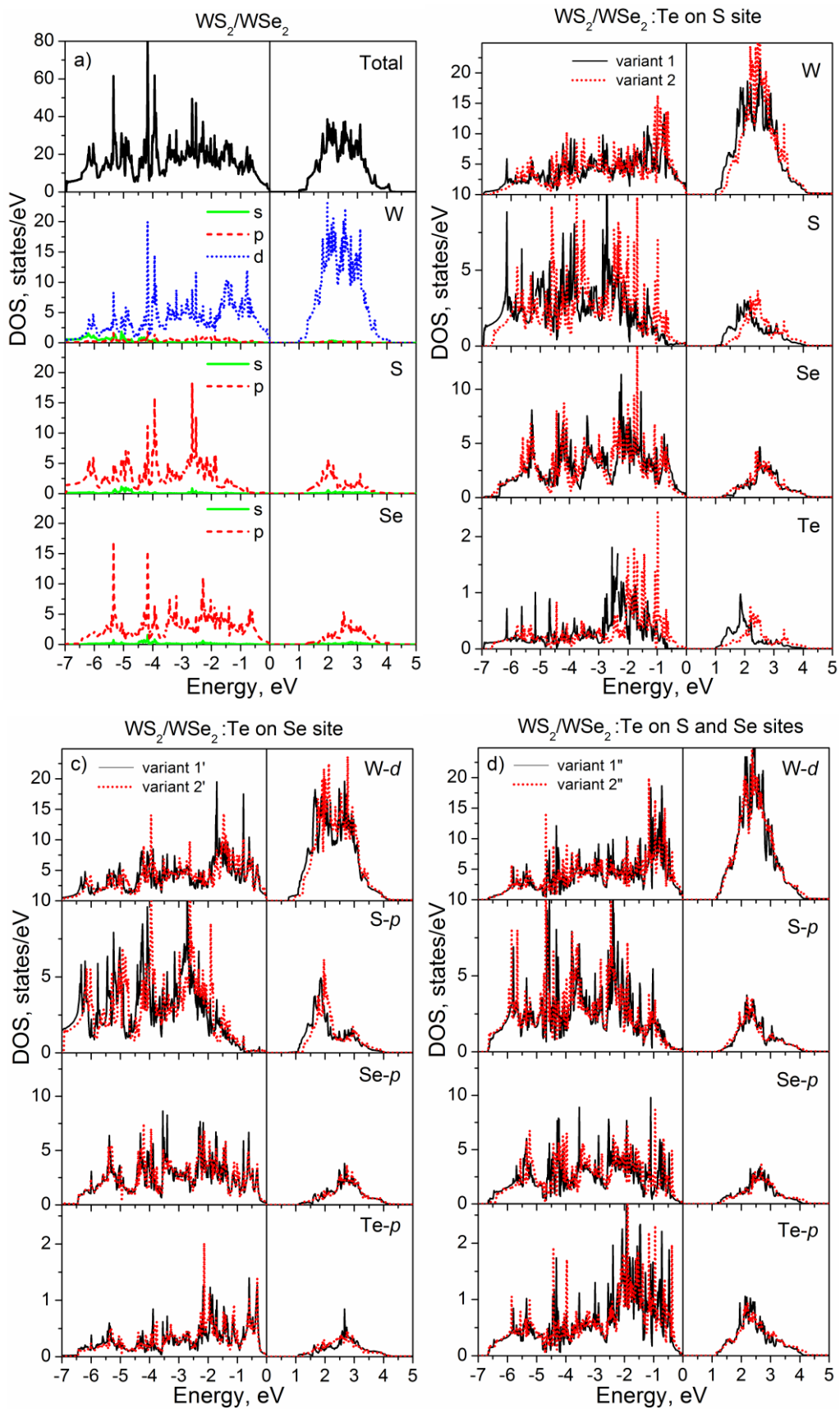
Figure 5 Total and partial DOS of pristine WS_2/WSe_2 heterostructure (a) and with Te atoms substituting S (b), Se (c) and S and Se atoms (d). Zero on the energy scale corresponds to the top of the valence band

Fig. 5 shows the total and partial densities of electronic states (DOS) for the pristine WS_2/WSe_2 heterostructure (a) and for two different variants of chalcogen atoms substitution in the case of Te atoms in the S site (b), Se site (c) and both S and Se sites (d), which were chosen as the most prominent ones from each five variants. In general, the DOS spectra look similar for all the structures with the main impact of d-electrons of W and p-electrons of chalcogen atoms. The presence of Te atoms does not lead to very prominent changes in DOS, and resulting mostly in very moderate shift of densities reflecting gap modification owing to lattice distortion.

CONCLUSION

The effect of substitution of S or Se atoms by Te ones on electronic properties of WS_2/WSe_2 heterostructure was studied by means of theoretical modeling. In all the cases considered the heterostructure preserved semiconductor properties, whereas the first gap changed its nature from direct to indirect depending on the position of substituting atoms and the distance between them. The heterostructure with Te atoms in the positions of Se ones preserves a direct gap, while substitution of S atoms leads preferably to an indirect-gap behavior. The band gaps in the variants when Te substituted both S and Se atoms change in a different way and their values strongly dependend on the mutual location of the tellurium atoms. Such peculiarity gives a new insight of ordering effect for stacking of two-dimensional transition metal dichalcogenides and its impact on the direct/indirect nature of the band gap and its value and opens the prospects for band-gap engineering and creation of multilayered structures with tuned gap, which is extremely important nowadays for development of novel electronic and photonic devices.

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COMPLIANCE WITH ETHICAL STANDARDS

This manuscript has not been published and is not under consideration for publication elsewhere. The authors declare there is no conflict of interest.

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