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# ALTERNATIVE II-IV-V<sub>2</sub> AND Zn-III-IV-As<sub>3</sub> COMPOUNDS FOR PHOTOVOLTAIC APPLICATIONS

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The electronic and optical properties of A<sup>II</sup>-B<sup>IV</sup>-C<sup>V</sup><sub>2</sub> and Zn-III-IV-As<sub>3</sub> semiconductors are investigated from first principles in order to find the ways of management their band gaps and lattice constants upon variation of its composition. The materials with the best fitting to semiconducting substrates are determined from the whole suite and recommendations upon practical application of such materials on the base of analysis of theirs reflectance and absorption spectra are given.

## INTRODUCTION

Search for alternative and renewable sources of energy requires materials of low cost with new electronic and optical properties. Nowadays photoelectric solar energy converters attract a special attention of world community. Stable II-IV-V<sub>2</sub> compounds weakly lattice mismatched with silicon or gallium arsenide can be potential candidates for photovoltaic devices. Some compounds among II-IV-V<sub>2</sub> and novel Zn-III-IV-As<sub>3</sub> alloys may be materials of interest in order to replace CuInSe<sub>2</sub> or CdTe for thin-film photovoltaic applications. From this point of view, main aspects for a semiconductor are absorption of light and photoelectric or photovoltaic effect [1]. Thus materials for solar cells should possess high absorption coefficient and have large direct band gap (~1.5 eV) to absorb in the range of the visible light. Moreover, if one wants to avoid expensive, rare, dangerous or too toxic elements and their derivatives used for thin-film deposition, it is better not to consider Cd-based and P-containing compounds. Indeed indium, selenium and tellurium are rare elements, cadmium is a heavy and hazardous metal, phosphorous is highly volatile, red-phosphorous burns, and phosphine gas is highly toxic. In this work we present the theoretical analysis of properties of II-IV-V<sub>2</sub> compounds, where II=Be, Mg, Zn; IV=Si, Ge, Sn; V=P, As, and Zn-III-IV-As<sub>3</sub> compounds, where III=Al, Ga; IV=Si, Sn.

The paper is organized as follows: first we analyze number of materials and chose those whose lattice constant is close to the silicon or gallium arsenide substrates. Then we calculate electronic properties, define materials with the preferably large direct band gaps and determine the optical properties of II-IV-V<sub>2</sub> and Zn-III-IV-As<sub>3</sub> semiconductors. For new Zn-III-IV-As<sub>3</sub> materials we also evaluate the changes in optical properties upon replacements of atoms of III and IV groups, from Al to Ga and from Si to Sn, respectively.

## METHOD OF CALCULATION

The structural, electronic and optical properties of II-IV-V<sub>2</sub> ternary and Zn-III-IV-As<sub>3</sub> quaternary sp<sup>3</sup> compounds were determined by VASP and WIEN2k *ab initio* simulation packages [2, 3] within density functional theory (DFT) using the generalized gradient approximation (GGA) of Perdew and Wang [4]. We

applied projector augmented-wave (PAW) method implemented in VASP code for structural optimization and calculation of lattice parameters. FLAPW method realized in WIEN2k code was used for calculation of band structures and optical properties. According to experiments [5], II-IV-V<sub>2</sub> ternaries are usually formed in body centered tetragonal structure, thus chalcopyrite-type crystal structure with 16 atoms was taken for simulation. Monoclinic lattice with 24 atoms in the unit cell was chosen for all Zn-III-IV-As<sub>3</sub> alloys. It was constructed from the experimentally observed Cu<sub>2</sub>SnS<sub>3</sub> monoclinic structure [6] in which group I atoms (Cu) are equally replaced by group II (Zn) and III (Al or Ga) atoms, group VI atoms (S) are replaced by group V atoms (As), and group IV atomic positions are unchanged.

## RESULTS

During the relaxation procedure it was revealed that ternary compounds remain in body-centered tetragonal structure while Zn-III-IV-As<sub>3</sub> quaternary alloys are considered to be monoclinic. Stability of compounds was evaluated by the calculation of the enthalpies of formation, which were found to be negative for all of them. Theoretically computed band gaps of II-IV-V<sub>2</sub> compounds in dependence of their lattice constants are presented on Figure 1. As it can be seen, lattice parameters of Zn(Si,Ge)P<sub>2</sub> are matched with silicon substrate, Zn(Si,Ge)As<sub>2</sub> or (Mg,Cd)SiP<sub>2</sub> compounds are found to be close to GaAs ones.

Band structure calculations show all studied compounds to be semiconductors. Most of them have direct-band gap located at the  $\Gamma$ -point with the values ranging from about 0.1 to 1.5 eV (Figure 1). It was found that band gaps for P-based II-IV-V<sub>2</sub> are higher in comparison with corresponding As-based ones. In the row Si-Ge-Sn, the gaps are the largest for Si-containing materials and the modified Becke-Johnson exchange-correlation potentials [8] will be tried in the future for an accurate determination of the band gaps.

However no experimental data are available on the electronic and optical properties of Be- and most of Mg-containing compounds for comparison of the results. Magnesium-containing compounds are found to be direct-gap semiconductors except MgGeP<sub>2</sub> which is quasi-direct gap semiconductor, and experimental data are available

only for  $\text{MgSiP}_2$  ( $E_g=2.0\text{--}2.26$  eV, direct gap) [9]. For zinc-containing compounds the experimental gaps are: for  $\text{ZnSiAs}_2$   $E_g=1.6\text{--}1.8$  eV (direct gap) [10–12], for  $\text{ZnGeAs}_2$   $E_g=1.15$  eV (direct), for  $\text{ZnSiP}_2$   $E_g=2.0\text{--}2.3$  eV (direct) [13–14], for  $\text{ZnGeP}_2$   $E_g=1.8\text{--}2.2$  eV (quasi-direct) [15].

This can be easily explained by the increase of the atom size in the row. One should take into account possible significant underestimation of the band gaps within DFT methods and may expect true gaps  $\sim 0.5$  eV larger than numerically computed. New functionals such the local Perdew-Burke-Ernzerhof exchange-correlation functional, the Heyd-Scuseria-Ernzerhof hybrid functional [7] or the smallest for Sn-containing ones.

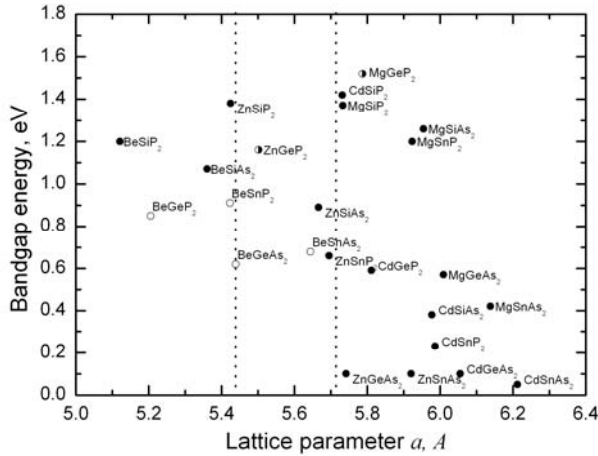


Fig.1. Calculated energy gaps of II-IV- $V_2$  compounds versus lattice parameters. Filled symbols – direct gap, open symbols – indirect gap, half-filled symbols – quasi-direct gap. Vertical lines correspond to lattice parameters of Si (left) and of GaAs (right).

The averaged reflectance spectra of some most perspective II-IV- $As_2$  ternaries are presented on Figure 2 in comparison with GaAs and  $\text{CuInSe}_2$ . One can see that the shapes of the obtained spectra are similar to the one of GaAs having reflectance greater than 0.4 in the visible range. Otherwise the spectrum shapes of the smaller gaps ternary compounds  $\text{MgSnAs}_2$  and  $\text{ZnSnAs}_2$  looks approaching the one of  $\text{CuInSe}_2$ ; although their reflectance remain higher around 1.5 eV and above.

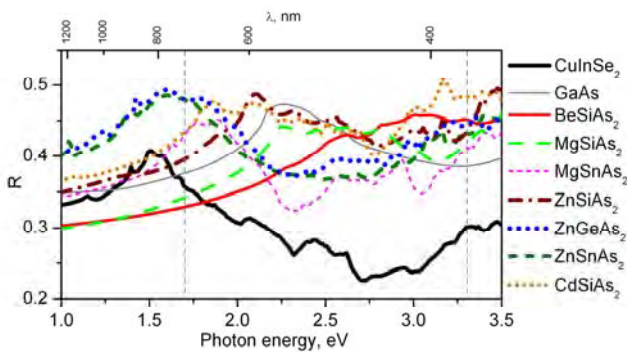


Fig.2 Averaged reflectance spectra of some II-IV- $V_2$  compounds compared with those of GaAs and  $\text{CuInSe}_2$ . Vertical lines correspond to the boundaries of visible spectral range.

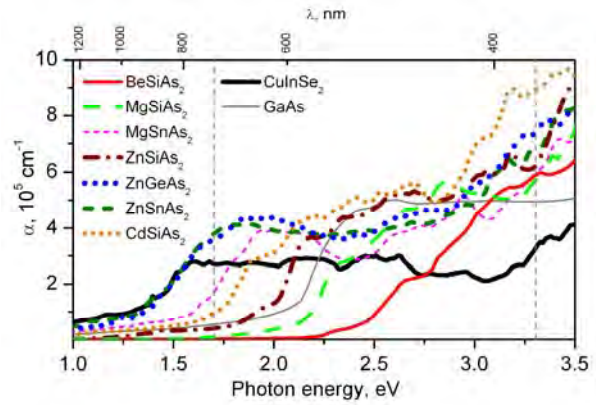


Fig.3. Averaged absorption coefficients of some II-IV- $V_2$  compounds compared with those of GaAs and  $\text{CuInSe}_2$ . Vertical lines correspond to the boundaries of visible spectral range.

In a general way, above their intrinsic absorption edges, the calculated absorption coefficients for investigated II-IV- $V_2$  compounds are comparable with those for widely used GaAs and  $\text{CuInSe}_2$ . The common tendency is that As-containing compounds possess higher  $\alpha$  value than P-containing ones. In the row Si–Ge–Sn, the absorption coefficients for Si-containing materials are the lowest while Sn-containing chalcopyrites have the largest  $\alpha$  values and the smallest band gaps. Nevertheless the values of  $\alpha$  are close to the one of GaAs and  $\sim 1.5\text{--}2$  higher than those for  $\text{CuInSe}_2$  at photon energies upper 2 eV (Figure 3). Above  $\sim 1.5$  eV, absorption coefficients of  $\text{BeSnAs}_2$ ,  $\text{BeGeAs}_2$ ,  $\text{MgSnAs}_2$ ,  $\text{ZnSnAs}_2$ ,  $\text{CdSnAs}_2$  and  $\text{CdGeAs}_2$  compounds demonstrate larger magnitude than those of  $\text{CuInSe}_2$ , although both  $\text{BeSnAs}_2$  and  $\text{BeGeAs}_2$  are indirect-gaps while Cd- containing compounds have predicted small gaps. Unfortunately, most of Be- (and Mg-) containing compounds have not been experimentally synthesized (except  $\text{MgSiP}_2$ ) and measured, probably because Be and Mg are light elements not easy to handle: Be forms very poisonous compounds and Mg metal burns in air. Thus multicolour solar cells with heterostructures close lattice matched to GaAs and built on thin-films of ternary compounds of the Zn-IV- $As_2$  family appears a promising solution.

Further, we have investigated the new class of Zn-III-IV- $As_3$  alloys. Here different variants of substitution of group III or IV atoms, namely  $\text{ZnAlSi}_{1-x}\text{Sn}_x\text{As}_3$ ,  $\text{ZnGaSi}_{1-x}\text{Sn}_x\text{As}_3$ ,  $\text{ZnAl}_{1-x}\text{Ga}_x\text{SiAs}_3$ , and  $\text{ZnAl}_{1-x}\text{Ga}_x\text{SnAs}_3$  are considered in order to tune both the lattice constants and the band gaps.

For Al-containing Zn-III-IV- $As_3$  quaternary alloys band gaps are larger when compared with Ga-containing ones. Similarly, quaternary compounds with Si as IV group element have larger band gaps than those with Sn. All quaternary compounds were found to be stable in simple monoclinic lattice with 24 atoms in unit cell and angle  $\beta \approx 108^\circ$ . Band structure calculations demonstrate semiconducting nature of all Zn-III-IV- $As_3$  compounds considered. No experimental data concerning this class of materials are available. Most of the compounds are characterized by a direct band gap band located at the center of the simple monoclinic Brillouin zone with the maximum values of about 1.3 eV for  $\text{ZnAlSiAs}_3$  (Figure

4a). Zn-III-Sn-As<sub>3</sub> compounds are practically gap-less. The variation of IV group element from Si to Sn drastically changes the band gap and lattice constants values: the gap values become smaller while *a* lattice constant rises up (Figure 4b), in a way comparable to the respective change of gap (-0.8eV) and lattice (+4.4%) between ZnSiAs<sub>2</sub> and ZnSnAs<sub>2</sub>. The change of III group element from Al to Ga does not affect the lattice constant but at the contrary of Al<sub>1-x</sub>Ga<sub>x</sub>As alloys it lowers the band gap insignificantly (~0.25eV). Indeed this result is not surprising as III elements occupy only 4 atomic sites in the 24 atoms monoclinic cell while they occupy half of the atomic sites in the III-V cubic lattice.

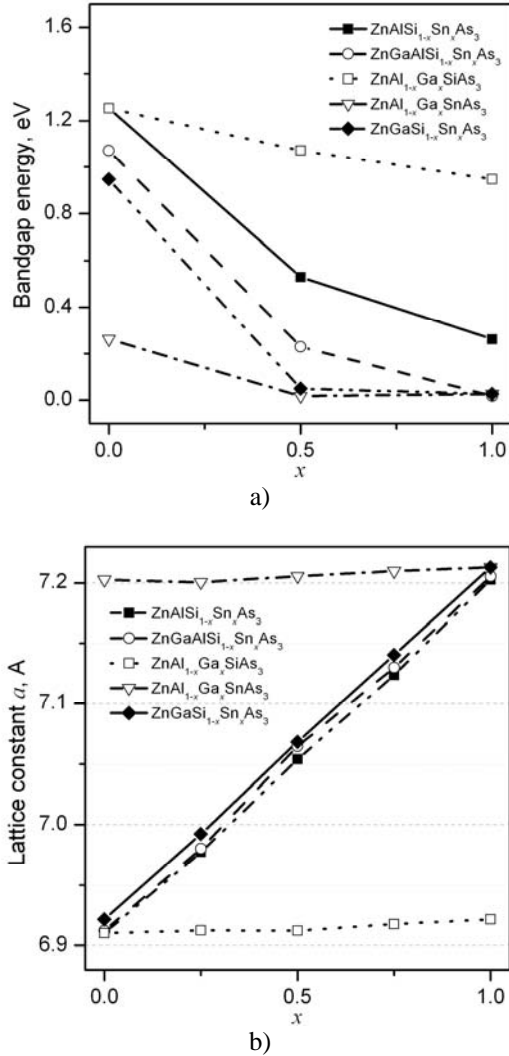


Fig.4. Band gaps (a) and *a* lattice constants (b) of some Zn-III-IV-As<sub>3</sub> compounds. The *c* lattice constants differ not more than 0.2 %.

Absorption coefficients of Zn-III-IV-As<sub>3</sub> demonstrate similar order of magnitude upon different substitutions (Figure 5a, b). Despite the fact that  $\alpha$  coefficients of compounds with Sn in IV sites are closer to CuInSe<sub>2</sub> characteristics, especially in the range of low energies, and coefficients of compounds with Si atoms are approaching to GaAs ones, generally absorption coefficients do not show considerable changes when Ga atoms are replaced by Al ones or Sn atoms substitute Si ones.

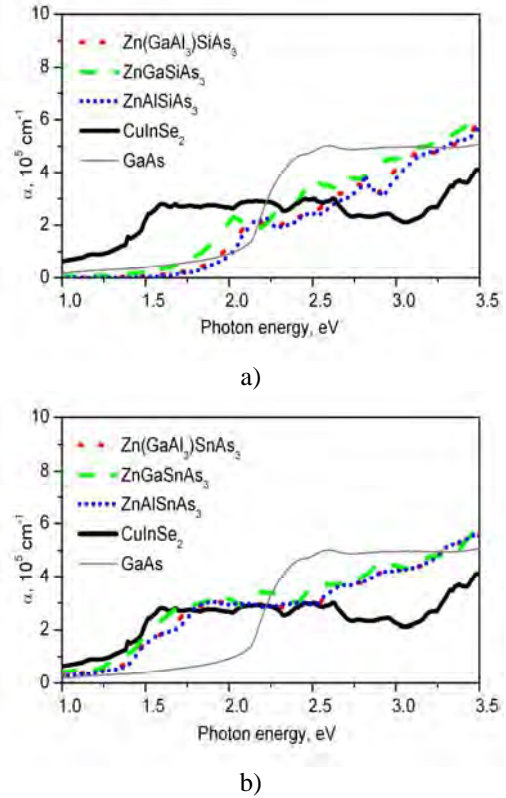


Fig.5. Averaged absorption coefficients of some Zn-III-IV-As<sub>3</sub> compounds with Si (a) or Sn (b) in comparison with CuInSe<sub>2</sub> and GaAs.

## SUMMARY AND CONCLUSION

This work is devoted to investigations of II-IV-V<sub>2</sub> and Zn-III-IV-As<sub>3</sub> compounds, which were found to be semiconductors. Ternary compounds exist in a body-centered tetragonal chalcopyrite structure, whereas Zn-III-IV-As<sub>3</sub> quaternaries are found to be stable in monoclinic lattice. Most of the materials (except Be-containing compounds) possess the direct-band gap located at the  $\Gamma$ -point with the gaps ranging from about 0.1 to 1.5 eV. The band gaps in P-containing compounds show to be larger than those in As-containing ones. Nevertheless, among materials of II-IV-V<sub>2</sub> class, arsenic compounds are easier to be obtained experimentally in comparison with phosphorous-based ternaries. The absorption spectra of Zn-III-IV-As<sub>3</sub> compounds are close either to CuInSe<sub>2</sub> or GaAs and do not show considerable changes upon substitution of either III- or IV group elements.

One of the possible ways to increase the quantum efficiency of solar cells is the formation of the multilayered heterostructures consisting of semiconducting materials with different band gaps, like combinations of II-IV-V<sub>2</sub> ternary or Zn-III-IV-As<sub>3</sub> quaternary compounds. From the whole investigated suite of II-IV-V<sub>2</sub> compounds only the Zn-IV-As<sub>2</sub> family seems to be perspective for multicolor heterostructural solar cells as their lattice constants are well matched to GaAs, their band gaps are large enough, their absorption coefficients values are comparable with those of CuInSe<sub>2</sub>. Moreover the Zn-IV-As<sub>2</sub> class is composed of rather cheap, abundant and non-toxic elements that make this class of materials potential candidates for photovoltaic applications with ability to replace CuInSe<sub>2</sub>.

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