[logo] INTiBS PAN
[Institute of Low Temperature and Structure Research of Polish Academy of Science]

Wrocław, 19.04.2023

dr hab. inż. Maciej Winiarski *[Ph.D. Eng., postdoctoral degree holder]*
tel.: +48 71 3954 131, e-mail: m.winiarski@intibs.pl
Włodzimierz Trzebiatowski Institute of Low Temperature and Structure Research
of the Polish Academy of Science
ul. Okólna 2, 50-422 Wrocław

Review of the doctoral dissertation of Ghulam Hussain, M.Sc., entitled:
"Investigating the electro-optical properties of 3D superlattices and 2D materials: A DFT study"

The doctoral dissertation of Ghulam Hussain, M.Sc., entitled: "Investigating the electro-optical properties of 3D superlattices and 2D materials: A DFT study" was written at the Institute of Physics of the Polish Academy of Sciences under the supervision of dr hab. Carmine Autieri *[Ph.D., postdoctoral degree holder]* (professor of IFPAN) and Dr. Giuseppe Cuono *[Ph.D.]*. The dissertation is in the form of a summary of a series of 4 publications, i.e. a general introduction and description of the methods used, followed by a short summary of the published results.

The first chapter begins with a broad historical introduction to infrared photodetectors. It is followed by subsequent subchapters in which the motivation for research as part of the doctoral dissertation is presented clearly and accurately. The advantages of devices using semiconductor quantum wells and the great interest of the scientific community in materials with a two-dimensional (2D) structure, mainly transition metal dichalcogenides (TMDC), are described. Thanks to these compounds, photodetection systems can be manufactured at the nanoscale and show excellent quantum efficiency. A particularly interesting object for scientific research may be Janus phases, i.e. 2D hybrid materials in which atomic monolayers contain various chalcogenide ions in a vertical orientation (unlike in the case of multilayers and superlattices). This chapter also presents the structure of new 2D nitride and phosphide materials with a complex multilayer structure of the unit cell.

The second chapter introduces the basic assumptions of the density functional theory (DFT). The use of the plane wave database and the pseudopotential method are described. Unfortunately, this chapter does not contain a description of the key correlation-exchange functionals used

in the research conducted by the Ph.D. candidate, i.e. what form the meta-GGA (MBJLDA) and hybrid (HSE) functionals are. No expansion of the abbreviations used and no literature references are given. It is also worth noting that the Author uses the statement "relativistic density functional theory" in his dissertation and publication, but he does not define it. An inquisitive reader can find the relevant literature on correlation-exchange functionals and guess that these were not standard calculations in the scalar relativistic formalism, but in the case of scientific studies such understatements should not take place.

The third chapter constitutes an abstract and a brief summary of the results of the publication series. The first paper investigated the electronic structure of the semiconductor InAs/$InAs_{0.625}Sb_{0.375}$ superlattice. This material shows the location of the bottom of the conduction band and the top of the valence band, characteristic of type II quantum wells. The complex electronic structure of the superlattice for various lattice parameters (for InAs, GaSb, AlSb substrates) was discussed. The superlattice shows a clearly narrower band gap than InSb. Doping with Sb ions leads to a modification of the top of the valence band and a strong increase in infrared absorption compared to the bulk InAs crystal. The tested multilayers have the potential to be used in far infrared detectors.

The results presented in the first paper required large-scale calculations. Determination of optical spectra is a particular difficulty in such cases. Although the composition of the superlattice (InAs/$InAs_{0.625}Sb_{0.375}$) was dictated by the available experimental data, the effects related to the change in the size of individual layers and the differentiation of the Sb content would be worth considering. The computational cost of such studies in the case of a slight reduction in the size of the computational cell or removal/addition of the Sb ion (changes in symmetry) would be relatively low. Considering the clearly non-symmetric effective masses determined for InAs using the MBJGGA functional (Table 1 in the first publication), it would be worth commenting with the help of current literature (e.g. M. Laurien, O. Rubel, Phys. Rev. B 106 (2022) 045204) that the use of this functional to determine the effective masses for such large and anisotropic systems as superlattices is debatable.

In the next paper, the electronic structure of XSi_2N_4 nitride materials (where X = Ti, Mo, W) was investigated, showing a strongly anisotropic, multilayer structure of the unit cell and predicted band gaps of 2.35-2.60 eV. The properties of the heterostructures of the above-mentioned materials, built in a vertical orientation (as in multilayers) and in a horizontal orientation (as part of a monolayer), were also considered. Calculations

of photon spectra were performed to confirm the thermodynamic stability of the tested systems. It has been shown that such new 2D nitride materials may be of interest for optoelectronic applications.

After analyzing the above results and discussing them, many open questions remain. It is hard to imagine an experimental technique that can produce such horizontal heterostructures with ions arranged in arbitrary parallel lines. Intuitively, materials with a checkerboard arrangement seem to be better and should be treated as solid solutions. In the case of vertical heterostructures, the effect of van der Waals bonds on the results of electronic structure calculations should be additionally considered. It seems that for nitrides, other than hexagonal BN, they are not crucial, but the existence of such bonds is clearly emphasized in the literature on XSi_2N_4 materials (probably due to the analogy to transition metal dichalcogenides). Given experimental data published by Hong, Y.-L. et al., Science 369 (2020) 670, the $MoSi_2N_4$ band gap was estimated at 1.94 eV, which is wider than the GGA results and clearly narrower than the HSE results. Therefore, the statement that hybrid exchange correlation functionals improve the results of electronic structure calculations for this class of materials is highly debatable. It would be worth following the literature on the possible influence of excitons (D. Liang et. al., Phys. Rev. B 105 (2022) 19530) on the electronic structure of XSi_2N_4 systems. Is there some similarity to the well-known transition metal dichalcogenides? The assumption that the investigated XSi_2N_4 systems can be good thermoelectrics is also questionable (transport calculations should be performed, carrier relaxation time should be estimated, etc.).

The next paper is an extension of previous studies on $MoSi_2N_4/XSi_2N_4$ horizontal heterostructures (where X = W, Ti). It showed a strong effect of biaxial strain/stress on the band gap width, which directly translates into the optical properties of such materials. This paper also demonstrated the thermodynamic stability of the tested systems by the analysis of phonon spectra. Although this trend is very popular in the literature, it should be emphasized that the fulfillment of any theoretical conditions (rules of chemical bond formation, as well as mechanical, thermodynamic, and energetic stability, etc.) does not mean that the synthesis of a given material is possible. The impact of non-equilibrium conditions should be considered similarly, because structural phase transitions that go beyond the symmetry imposed in the DFT calculations are possible.

The last paper in the series concerns the electronic structure of the Janus phases $MoGeSiP_2As_2$ and $WGeSiP_2As_2$, which are hybrid materials composed of

(Mo;W)Si_2P_4 and (Mo;W)Ge_2As_4 monolayers. Monolayers of such systems do not have reflection symmetry in the direction of the Z axis, which leads to a complex electronic structure and the Rashba effect. The analysis of non-collinear spin ordering near the valence band peaks and the discussion of the potential application of such materials in spintronics seem to be of particular interest. Analogous studies have recently been carried out for transition metal dichalcogenides due to similar spin splitting in the conduction band valleys (hence the name valleytronics popular in the literature).

In the case of Janus phase studies, the conclusions regarding changes in output work caused by the lack of reflection symmetry in the direction of the z-axis are highly debatable. The standard calculation procedure for such systems requires the use of the so-called dipole correction, thanks to which the potential forced by periodic boundary conditions on the edges of the calculation cell is equalized. Otherwise, the tested system is subjected to artifactual influence, which may undermine all results and conclusions. This is a particularly important issue in the case of surface physics research and the software used by the Ph.D. candidate (VASP), which provides such an opportunity. This oversight is all the more surprising as the dipole correction is commonly used in the literature on Janus phases (e.g. W. Zhou et al., Phys. Rev. B 99 (2019) 075160).

Ghulam Hussain's dissertation takes 79 pages, including the content of 4 publications and supplementary materials, which seems not very extensive but is acceptable in the form of a summary of a series of publications. The paper was written with attention to editing details, although there were minor omissions in both the paper and the publications (e.g. in the caption of Fig. 5 in the second publication, the Fermi energy is partially confused with the Fermi level). The whole text is legible and grammatically correct, which obviously facilitates the analysis and evaluation of the presented results.

The research conducted by the Ph.D. candidate is part of the current trend in the scientific community related to the long-term interest in 2D materials. The systems considered in the doctoral dissertation have a more complicated crystal structure than the popular transition metal dichalcogenides, which made the computational costs and technical difficulties related to obtaining numerically correct electronic structure results for them relatively high. Publications in the series have appeared in prestigious journals with a significant impact factor. The Ph.D. candidate is the lead author in all the papers, and, taking into account the statements of the co-authors, he obtained the presented results himself. The Ph.D. candidate also has scientific achievements that go beyond the results presented in the dissertation.

Despite numerous comments, the doctoral dissertation of Ghulam Hussain, M.Sc., in my opinion, meets all the quantitative and qualitative criteria for doctoral dissertations in the field of exact and natural sciences in the discipline of physical sciences. In connection with the above, I request that Mr. Ghulam Hussain, M.Sc., be admitted to the next stages of the doctoral procedure.

[illegible signature]

dr hab. inż. Maciej Winiarski *[Ph.D. Eng., postdoctoral degree holder]*

Instytut Niskich Temperatur i Badań Strukturalnych **Institute of Low Temperature and Structure Research**
im. Włodzimierza Trzebiatowskiego Polskiej Akademii Nauk of Polish Academy of Science

• ul. Okólna 2, 50-422 Wrocław | Poland • tel.: +48 71 343 5021 • intibs@intibs.pl • www.intibs.pl