Summary

Present thesis entitled *'Energetics, Structural and Optoelectronic Properties of III-V Semiconductor Heterostructure Nanowires'* presents the results on the computational investigation of fundamental ground state structural, electronic and optical properties of selected III-V compounds for their bulk polytypic phases and two-dimensionally confined nanowire (NW) configurations. Followed by the deep assessment of the proposed properties in the bulk and NW configurations, the relevant systems are filtered and selected for construction and investigation of the heterostructure nanowires (HSNWs). The investigation of all considered materials is performed within the umbrella of *first-principles* density functional theory (DFT) approach. This theory as a quantum mechanical tool has emerged as an all-in-one solution to many-electron problems and is famous for providing better prediction of the ground state properties of materials. Moreover, various pseudopotentials constructed under wide range of exchange and correlation functionals have established paramount attention to this theory owing to their ability to treat materials ranging from insulating to semi-conducting to highly correlated materials.

The significance of the III-V materials in the latest cutting-edge technologies cannot be overruled. Being the central subject of the thesis, the relevant literature and findings are discussed in the first chapter. These materials under their bulk and modified conditions have been considered to be of great importance due to their spatial electronic dispersion curves and bandgap magnitudes. The different techniques like chemical doping, external strain, quantum size effect and heterostructuring have been observed as the efficient methods to obtain tailor made properties of the systems and

desired carrier dynamics through them. The chapter sets-up a link between the past and present research areas in which the III-V materials have been exposed and ways of utilization. Motivated from the benchmark results attained by the III-V materials and to fill-up the gaps within the existing literature, we have investigated structural, electronic and optical properties of selected III-V compounds under ambient and modified conditions using the DFT approach. The application of external strain and quantum size effect have been considered as the major parameters for tuning the electro-optic transport through the systems.

Followed by the inspiring findings on III-V materials and formulating the objectives of the thesis, next task was to ***implement*** the proposed research study within the DFT framework. The hierarchal tree of the DFT approach and the development of two major exchange and correlation functionals that are majorly used for studying the ground state properties of the materials has been described in ***Chapter*** 2. A brief review of development of the DFT approach to the different approaches that have been utilized to treat phonon and photon related phenomena like vibrational and optical properties respectively have been described. The famous opensource pseudopotential-based plane-wave package QUANTUM ESPRESSO and relevant plug-in packages were utilized for computation of the proposed properties.

We have selected two famous elements from group-III elements; i.e., aluminium and gallium. These two elements with the combination of pnictide group were considered for investigating their ground state properties under bulk and nano regimes. The first system, i.e. gallium pnictides (GaX: X=P, As, Sb) were investigated for their ground state structural, electronic, vibrational and thermoelectric properties and the

respective results have been described in ***Chapter*** 3. Followed by the crystal phase (cubic zincblende and hexagonal Wurtzite) dependent properties of the GaX compounds, the two-dimensionally confined geometry was introduced in all three compounds with hexagonal WZ phase so as to construct 1D NWs. The 1D NWs of all three compounds were then considered for studying the effect of external strain and size modulation on their electronic properties. Fig. 7.1 represents the optimized crystal structure of gallium phosphide (GaP) NW with three distinct diameters and, the figures on the left and right side of the crystal structures show the effect of uniaxial compressive strain and size on the electronic dispersion of the NWs. It is clearly observed from the figure that the electronic nature of the GaP under NW configuration transforms from indirect to direct under the strain magnitude of 2% and NW diameter of ~ 3nm. Similar results are observed in case of remaining GaX compounds under

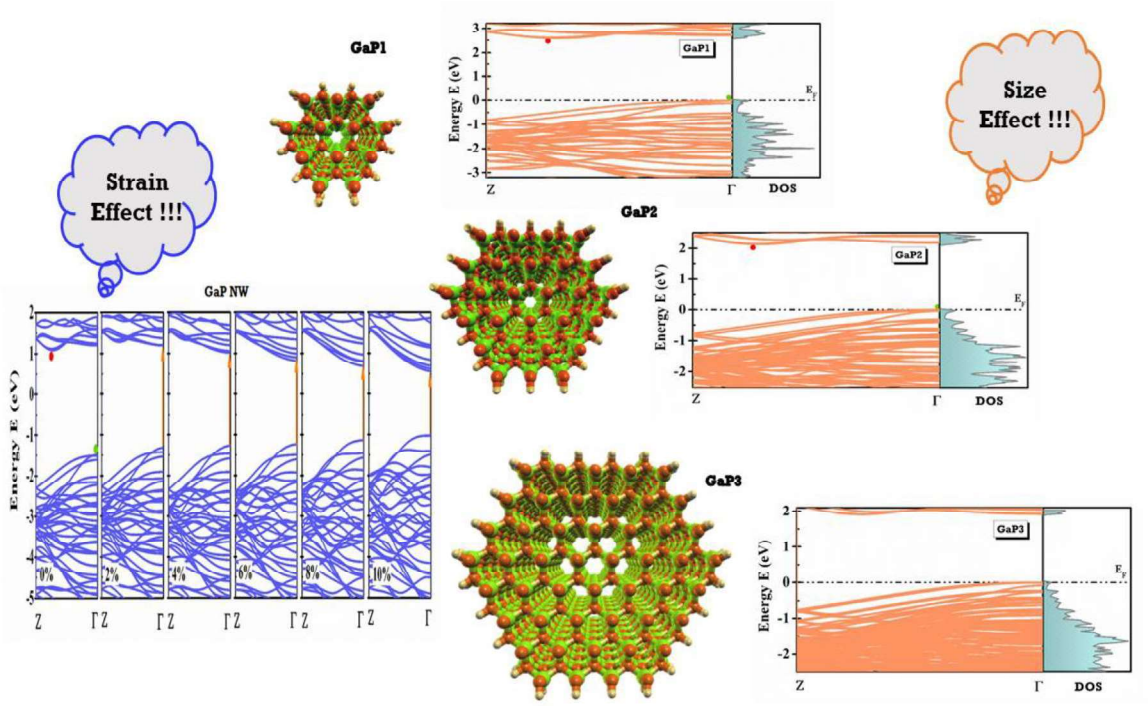

Figure 7.1. The computed electronic band structures of GaP NWs under the effect of external strain and size modulation.

different strain magnitude; however, the effect of size does not modify the indirect nature of the GaAs and GaSb NWs.

Followed by this study, the construction of heterostructure (HS) from the optimized GaX NWs was done and the radial HSNWs with core/shell geometry were constructed keeping GaSb NW fixed as the core NW. The so formed GaSb/GaP and

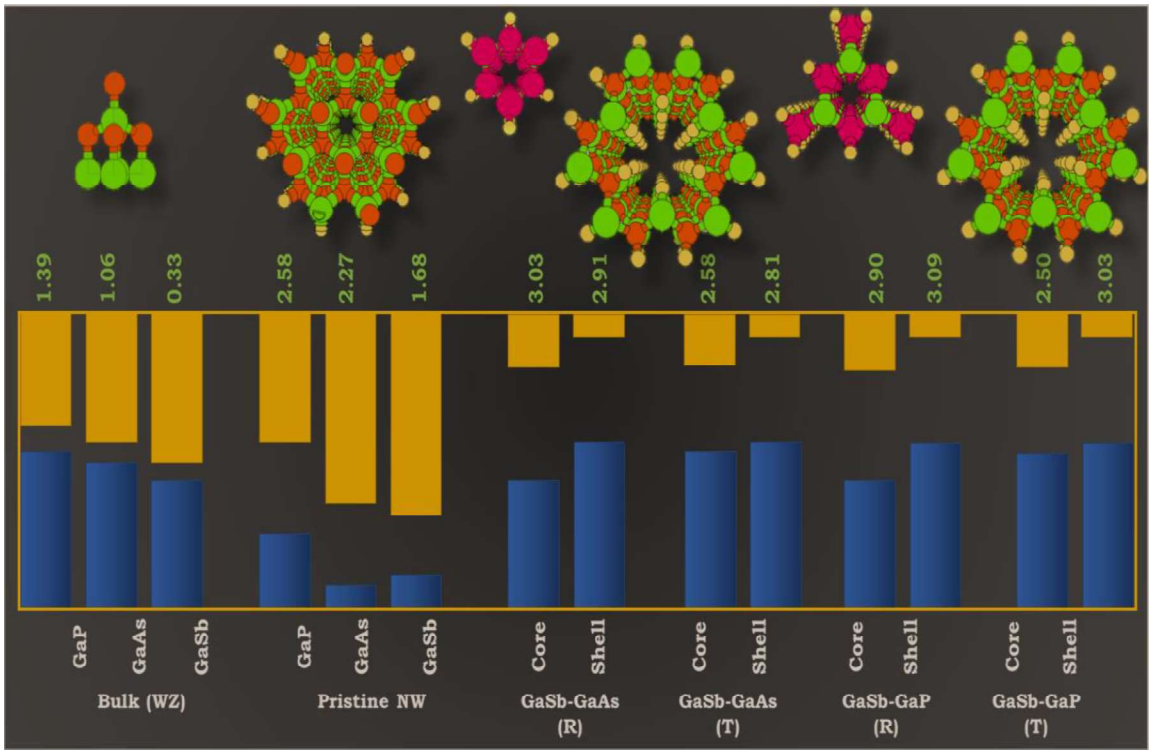

Figure 7.2. Schematic representation of band edge alignments (not to the scale) of GaX (P, As, Sb) in bulk and NW forms and for core and shell NWs of corresponding HSNWs with GaSb NW as a shell NW (The schematic diagram on the top represent the crystal structures of the systems under bulk, NW and HSNWs dissected into core and shell structures with corresponding electronic band gaps in eV).

GaSb/GaAs HSNWs were studied under two distinct core shapes; i.e. the core GaSb NWs were constructed with round (R) and triangular (T) cross-sections and in total four different HSNWs were investigated for understanding their electronic and optical properties. The Figure 7.2 shows the comparison between the computed electronic band alignments of GaX (X=P, As, Sb) compounds under bulk and NW configurations together with the four considered HSNWs. It is evident from the figure

that all four HSNWs possess type-II band alignment with moderate gap (1.83-1.91 eV) which is the unique characteristic desired in optoelectronic and photovoltaic device industry due to their spatial ability of controlling charge carrier dynamics thereby improved efficiency. Furthermore, out of the four HSNWs, the GaSb/GaP (R) system possesses direct nature of bandgap which acts as a cherry on the cake! The spatial band alignment and the desired electro-optic response of the HSNWs provided motivation to investigate their solar cell parameters for testing their applicability in photovoltaic devices. The computed power conversion efficiency of 32% was observed in case of pristine GaSb NW with ~ 2 nm diameter, and under heterostructured configuration, the GaSb-GaAs HSNWs possess higher efficiency (18%) than the GaSb-GaP HSNWs (16%). The spatial band alignment with moderate electronic band gap results in markable solar cell performance of the systems and further insight to the photovoltaic response can be achieved under spectroscopic limited maximum efficiency (SLME).

After complete study of GaX compounds under bulk, nanowire and heterostructure nanowire configurations, the next system, i.e., AlX (X=P, As) compounds were considered for investigating their opto-electronic properties. The results of AlX compounds ranging from their bulk phases to nanowire and to the radial (R) and axial (A) heterostructured configurations are thoroughly discussed in the present thesis at appropriate place. The results suggest both compounds under bulk phase possess moderate electronic bandgap that lies within the optical regime of the electro-magnetic spectra, yet the indirect nature in both phases suggests contributions from the non-radiative processes reduce the absorption capacity of the systems.

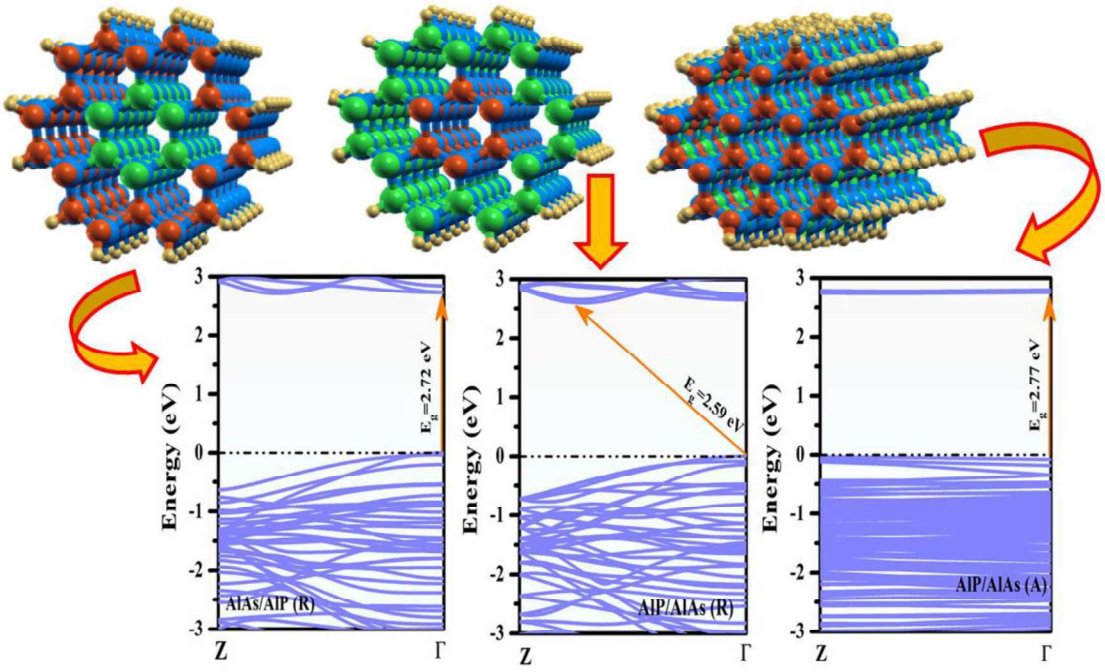

Figure 7.3. Optimized crystal structures of AlAs/AlP (R), AlP/AlAs (R) and AlP/AlAs (A) HSNWs with their corresponding electronic dispresion curves.

Moving to NW configuration, the AlP compound shows indirect to direct bandgap transition, and the gap magnitude of both systems show significant enhancement due to quantum size effect. Moving to radial (R) and axial (A) HSNW configurations, the constructed three HSNWs, AlP/AlAs (R), AlAs/AlP (R) and AlP/AlAs (A) show spatially aligned band edges with type-II configurations. Furthermore, out of the three, the AlAs/AlP (R) and AlP/AlAs (A) HSNWs possess direct bandgap (2.71 and 2.74 eV). These two qualities make these systems suitable for high-energy photon (visible-to-ultraviolet regimes) absorber layers in photovoltaic devices. Apart from the photovoltaic devices, these systems also qualify for the optoelectronic devices that operate within high-energy regime.

In the end, we have studied two phosphide NWs; BP and GaP for testing their applicability in the field of latest cutting-edge energy application of producing

hydrogen via splitting of water molecules. As it well-known, the hydrogen being the lightest element possesses immense power and can be utilized as a fuel to produce clean energy; i.e. the fuel that is eco-friendly and non-hazardous to environment. The considered two NWs were investigated for understanding their ground state electronic properties followed by the adsorption of hydrogen/oxygen on the NW surfaces. The investigation of adsorption and Gibbs free energy profiles provide insight to adsorption mechanism and probability of utilizing the systems as the hydrogen evolution reaction (HER)/oxygen evolution reaction (OER) catalyst under hydrogen/oxygen adsorption. As observed, both compounds, i.e. boron phosphide (BP) and gallium phosphide (GaP) under two-dimensional confinement show enhancement in the gap magnitude with the transformation of the bandgap nature from indirect to direct. Both NWs were subjected to substitutional doping so as to tune their electronic and adsorptive properties. In case of BP NW, the bandgap reduces from 2.96 eV to 2.87 eV on introducing Ga-substitution; this also improves the OER activity of the NW as compared to the pristine conditions. On the other hand, the GaP NW incorporation of boron in GaP NW improves HER activity of the NW via reducing the electronic bandgap from 3.8 eV to 2.5 eV. The reduction occurs due to the origin of the impurity states near the valence band regime in the presence of boron atom replacing the gallium atom in the host NW. The OER activity of the GaP NW is not promising limiting the applicability of the GaP NW for HER catalyst. In a nut-shell, the present study suggests a path-way to tailor the electronic and catalytic properties of the III-V semiconductor materials. The presence of global warming and energy crisis demand the development of non-toxic and eco-friendly materials that can

generate energy in a cleaner way. The present study can be considered as one of the stepping stone of the new era!

Future Scope

The present trend of the materials development for energy applications indicate a great need of evolution in the material design for optimizing the efficiency. The techniques usually focus on the tuning of the charge carrier/photon/phonon transport of through the materials as per the relevant application. Apart from the technique development, the either way is to design novel materials; within just a span of a decade, the material scientists, researchers and engineers have developed high-throughput methods to screen the materials form the database and design unique materials utilizing artificial intelligence assisted tools. My future scope shall be a connection between my present knowledge of methods for studying material properties with my future contributions to material science using pre-existing and advanced theoretical techniques together with the relevant computational tools.

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