First-Principles Study on Crystal Phase Superlattice Nanowires Heterostructures

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Abstract. We perform a first-principles density functional theory study on structural and electronic properties of a series of crystal-phase heterostructure atomic-scale superlattice (SL) nanowires (NW) from GaN material, i.e. GaN wurtzite (WZ) / zincblende (ZB) material interface. The effects of surface/interface relaxation and surface stress which are absent in atomistic models are carefully taken into account. Structural properties, energy bands and electronic properties for a class of hexagonal wires with various period of SL structure and diameter size are discussed. Pseudo hydrogen atoms, i.e. hydrogen with partial charges, are used to passivate the dangling surface bonds, which remove the localized in-gap surface states and suppress the surface reconstructions. With this passivation procedure the band structure show the type II for all wires. While the electrical aspects of these SL nanowires are explored through density functional theory, their subsequent band structures are used to determine the thermoelectric properties via the Boltzmann transport theory. Finally, the thermoelectric properties dependence on temperature is unveiled.

1. Introduction
Nitride-based hetero-structure structured nanowires (NWs), either core/shell or superlattice (SL) heterostructure, i.e. of which parts are made of different nitrides material and/or different crystal phase, are promising for electronic and optoelectronic device applications, e.g., high-efficient, multicolor light emitting diodes [1, 2], solar cells [3], lasers [4]. Experimental works [1, 2, 3, 4, 5, 6, 7, 8, 9] and theoretical works [10, 11, 12, 13, 14, 15] indicate that various physical properties of these structures, especially the optical properties, can be tuned by several experimentally attainable parameters, including the size of the core/shell or SL period and diameter. This is one of the compelling advantages which fuel the broad interest on the structures. For a nano semiconductor structure, the surface reconstruction induced by the dangling bonds on the surface is essentially important and dramatically affects the structural and the electronic properties [16, 17, 18, 19, 20, 21, 22]. In case of a GaN SL crystal phase heterostructure nanowire, i.e. parts of wire with different structural phases along the nanowire direction, such as wurtzite (WZ) and zincblende (ZB) forms of the same compound, the WZ-ZB interface is another important factor. In addition, the quantum confinement in the SL NW is related to both the surface and the interface because the SL interface often form a type II
band-alignment (staggered gap) with electrons on ZB and holes on WZ [5, 23], thus for the carriers which are already confined by the surface, residing aside the interface is favorable. The WZ-ZB phase lattice mismatch, 1% on the plane perpendicular to the WZ wire growth direction [0001] [23], also plays a role. All of these factors, simultaneously existing in the GaN crystal phase heterostructure SL NWs, result in combined effects on the properties of the structure. We present in this paper a first principles study on the role of the surface/interface reconstruction in GaN WZ-ZB SL nanowires. Further by a combination of first-principles simulations, based on the density functional theory, and Boltzmanns semiclassical theory, we have calculated some transport and thermoelectric properties of the this SL NW.

This paper is organized as follow. In Section 2, we describe the SL NWs and a reference model in which the surface effects are suppressed. Details on the numerical method used in this works are then introduced in Section 3. Section 4 is used to justify the reference model with bandstructure and Density-Of-States (DOS) analysis. In Section 5, we discuss the obtained results for bandstructure derived the transport and thermoelectric properties and the role of the surface reconstruction. The paper is closed by Section 6 with some conclusions.

2. GaN/AlN SL NWs and their passivated NW model

The most common crystal phase heterostructure consists of hexagonal wurtzite (WZ) and cubic zincblende (ZB) polytypes. Resulting heterostructures are typical of type-II, i.e., a ZB inclusion inside a WZ matrix forms a quantum well confining electrons, while a WZ inclusion in a ZB matrix forms a quantum well confining holes. It’s noted that in the bulk materials, where inclusions of a different crystal polytypes inside a 3D matrix cannot be built and are typically surrounded by dislocations. In SL NW, crystal-phase heterostructures present several advantages with respect to compositional (i.e. from different materials) ones: (i) the abruptness of the heterointerface, coinciding with a single basal plane, (ii) chemical homogeneity, and (iii) the low lattice mismatch. Basal SFs can be regarded as a single cubic sequence of planes (ABC) in the hexagonal matrix (ABAB...) and are associated with a strong luminescence signal due to bound excitons at energy 3.41 – 3.42eV. For GaN SL NW the presence of ZB inclusions of different thickness in WZ GaN has only been reported in [24] and an analysis of thermo-electric of such structures has not been carried out.

The building block of the GaN WZ layers in this work is a WZ hexagonal base layer, which is being composed of several hexagonal rings of atoms enclosing the NWs axis, taken to be parallel to the WZ [001] direction (ab stacking sequence) or as z axis. A WZ hexagonal base consist of 24 atoms with diameter of 10.1Å (Fig1a). For ZB base layer a hexagonal shape of [111] cut-plane (abc stacking sequence) with suitable size is taken, so that a ZB hexagonal base consist of 25 atoms with diameter of 11.7Å (Fig1b). These shapes of nanowires are chosen in such a way as to minimize the number of dangling bonds on outer edge-layer atoms, that for WZ domain the outer layer atoms have a minimum coordination of three, leaving at most one dangling bond on the edge atoms. For ZB domain there are three hexagonal edge atoms with coordination number of two leaving two dangling bonds for each atomic layer (see last image on Fig. 1). There three edge Ga atoms on one atomic layer following by three N edge atoms on the next atomic layer successively, thus making a dangling bond density on the ZB region is significantly higher than in the WZ region. This lead to more contribution of ZB domain on the surface state and surface reconstruction.

It is mentioned that for a NW, the surface reconstruction is an important factor that strongly affects physical properties of the NWs. To estimate the effects from the surface reconstruction, for each NW, we study a reference NW in which a number of pseudo hydrogen atoms are used to saturate the dangling bonds, thus suppressing the surface reconstruction and thus maintaining nearly bulk bond angle and bond length for the outer surface atom layer. These are artificial hydrogenic atom with partial charge. i.e. a charge of 3/4e or 5/4e with e is electron charge,
depending on whether the dangling bond is on a nitrogen or gallium atom, respectively [22]. We call the reference NWs by _passivated_ NWs while the original NWs are called _unpassivated_ NWs. To passivate a WZ base layer one needs 12 suitable pseudo hydrogen atoms whereas for a ZB layer needs 15 atoms.

**Figure 1.** (Color online) From left to right: atomic scheme of relaxed GaN wurtzite (WZ) base layer; zinc-blende (ZB) base layer; real SL insertion WZ-ZB and a passivated SL NW with pseudo hydrogen. Beige sphere for Gallium atom, Blue and Cyan spheres correspond to N atoms in the WZ and ZB domains, respectively whereas white is pseudo hydrogen with partial charge (3/4) and light blue is pseudo hydrogen with partial charge (5/4) for passivation the dangling bonds.

**Table 1.** Summary of structure’s series of SL nanowires studied in this work, i.e., SL NW: A,B,C and their passivated SL NW: AH, BH, CH.

| Structure | Number atoms | Relaxed Length (Å) | Ratio WZ:ZB layer |
|-----------|--------------|--------------------|-------------------|
| _A_       | 122          | 13.13              | 3:2               |
| _B_       | 170          | 18.90              | 5:2               |
| _C_       | 196          | 21.7               | 4:4               |
| _AH_      | 188          | 13.59              | —                 |
| _BH_      | 260          | 19.01              | —                 |
| _CH_      | 304          | 21.73              | —                 |

**Figure 2.** (Color online) Relaxed unpassivated SL NW A and B viewed along wire direction. Color scheme as in Fig.1.
3. Computational details

We use in this work the version of density functional theory (DFT) implemented in SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms), the electronic structure code that implements linear-scaling methods for gapped systems [25, 26]. The flexible localized numerical double-zeta-plus polarization basis set is used, allowing arbitrary angular momenta, multiple radial functions per angular momentum, and polarized and off-site orbitals [26]. Some figures in this work are prepared by XCrySDen [27]. Norm-conserving Troullier-Martins nonlocal pseudopotentials with partial core corrections are used for our calculations. The valence electron configurations taken for nitrogen, and gallium atoms are $3s^2 3p^1$ and $4s^2 3d^10 4p^1$. Of these configurations, the gallium-3$d$ electron states are treated as valence states to describe the hybridization between the gallium-3$d$ and nitrogen-2$p$ orbitals. The pseudopotential radii employed in our calculations for $s$, $p$, $d$ and $f$ orbitals of nitrogen are all 1.14. Those for gallium are 2.1 au, 2.29 au, 2.1 au and 2.5 au, respectively. The pseudopotentials for the pseudo hydrogen atoms are generated from the pseudopotential of ordinary hydrogen atom using the fractional program implemented in Virtual Crystal Approximation, a tool provided by SIESTA 3.2, in which the pseudo hydrogen atoms are treated as the synthesized atoms. The Perdew-Burke-Ernzerhof functional [28] is used for exchange correlation energy of all the species.

The SL NWs structures are then optimized by minimizing the interatomic forces using selectively the conjugate gradient and the modified Broyden methods. The ground state energy and the optimized geometries of all NWs are carefully tested for convergence with respect to the size of the localized basis set and the dimensions of the supercell. The convergence is assumed when the forces on the atomic sites are less than 0.01 eV/Å. The shift-energy parameter related to the cutoff radii of the localized atomic orbitals is chosen to be 150 meV for obtaining the optimized theoretical WZ lattice parameter for GaN ($a = 3.184\text{Å}$ and $c = 5.186\text{Å}$). These values are consistent with the experimental lattice parameters of real GaN ($a = 3.189\text{Å}$ $c = 5.185\text{Å}$) [23]. For each NW, a system of two WZ and ZB domain in a box with the periodic boundary condition on the $z$ direction. The structure is wrapped by at least 10 Å of vacuum thickness along the $x$ and $y$ directions to avoid the interaction of the system with its periodical images. The box size in the $z$ direction, which is the lattice parameter $c$, is determined independently to minimize the total energy of the system.

Benchmarks of the passivated NW model, constructed with the pseudo hydrogen atoms, each of which is characterized by an artificial fractional charge, is used as the reference structure of which there is no surface reconstruction. We discuss some justifications for this model on detail in other work [22].

4. Electronic bandstructure and projected density-ofstate (PDOS) analysis

From the relaxed structures obtained in the previous Section, we have calculated the band structures and DOS of those SL NWs. To figure out the role and influence of the passivation procedure on Figure 3, the band structure of the unpassivated (Fig.3a) and passivated (Fig.3b) GaN-WZ nanowire are shown. Comparing to those of the passivated NW, the conduction band and the valence band of the unpassivated GaN-WZ are reconstructed with several new surface-induced states. For the conduction band, these states reside well just above the conduction band minimum (CBM) while for the valence band, the corresponding states are introduced right in the valence band maximum (VBM). In addition to the surface-induced states, there are also some small negative shifts on the other states of both the valence and the conduction bands. As a consequence of the surface-induced states, the band gap of the unpassivated GaN-WZ is dramatically reduced, i.e. from $2.51\text{eV}$ to $1.78\text{eV}$ (see Fig.3c for Pure WZ column on the right), as also addressed elsewhere, e.g., in Ref. [22, 23]. The Fig.3c also show the gap dependence on the WZ-ZB composition ratio of all the studied sample. For the passivated NW (upper solid line in Fig.3c) it well restored the Vegard’s rule for the bulk alloy composition, which corresponds to
the case without surface effects. However for the unpassivated case, i.e. with surface effect the situation is totally changed as there is introduction of many surface states inside the gap make that small diameter NW structure become almost gap-less. Here we should note that although DFT calculations systematically underestimate the band gap of semiconductors, a discussion on the band gap of the NWs here is reasonable.

Figure 3. (Color online) Band structure of the unpassivated GaN-WZ nanowire (a) and passivated GaN-WZ NW (b). Dashed black lines present the Fermi levels of the NWs. Dotted-line rectangles on the figure indicate the surface-induced states.

The prominent effect can be noticed here is band gap’s reduction due to the surface states as described above. The more surface states, i.e. depend on surface/volume as well as WZ/ZB ratio, the more band gap reductions. In Fig.4a the overlaying total DOS of unpassivated and passivated of a sample A was given, which shows that the sharp peak seen in the DOS of the NW is reduced from unpassivated to passivated case and the surface states reside both the VBM and CBM and mid-gap states. For the nature of the surface-induced states, we examine further the projected density of states (PDOS), i.e., the electronic density of states projected on particular orbitals or atom sites of the NWs. In Fig. 4b, plots for the density of states of the passivated and unpassivated (upper window) and passivated (lower window) projected on particular domain (WZ and ZB) and orbitals are shown. It reveals that because of the surface reconstruction, both the valence and conduction band are changed dramatically by surface-induced states. For the unpassivated NW, the surface states marked by the arrows are dominated at both CBM and VBM regions. In particular, the surface state from ZB domain, i.e. Ga−ZB and N−ZB are dominated (see Fig. 4B upper window). For VBM edge states N−ZB is more favor than Ga−Zn, where as for CBM edges the second come over. Within this the nitrogen 2p states dominate the VBM of N-ZB while contributions from gallium 4p states dominate the CBM with Ga−ZB and nitrogen 2s of N−ZB and N−WZ 2p and Ga−WZ 2p states are comparable in the CBM. For passivated NW, while the surface states are suppressed, the edges of VBM is dominated by the nitrogen 2p states of both N−ZB and N−WZ domains. For the CBM edges, Ga 4p of ZB domain almost dominated than N 2p ZB and N 2p and Ga 4p of WZ domain respectively (see Fig.4b lower window). Also it shows that without surface reconstruction, the gap gets wider and there are not a number of mid-gap states.

Figure 5 shows the spatial distribution of of two edges states at the VBM and CBM (the HOMO and LUMO) for unpassivated and passivated sample A. For passivated sample because the SL interface forms a heterostructure type II (staggered gap) of which both VBM and CBM of ZB-domain are smaller than of WZ-domain, edges state of the VBM are confined in the WZ-domain (left on second-row) where as edges state of CBM are confined in the ZB-domain (right image on second-row). The surface atoms make no contribution to these states since the surface reconstruction is suppressed by the present of pseudo hydrogen atoms, which have shown no contribution to VBM and CBM too.

The top row of Fig. 5 visualizes the dominant contribution of the surface-induced states to
the HOMO and LUMO as well as small contribution of atoms from core inside region. However it also can be seen that HOMO is more confined in the WZ region and LUMO in the ZB region as well. That result in a so-called charge-separation, i.e. when electronhole pairs will form by absorbed photon, this charge separation into electrons and holes at the interface’s vicinity of the WZ and ZB stacking will occur, and electrons will be located in the ZB region and the holes will located in the WZ region (see Figure 5).

Figure 4. (Color online) (a) Total DOS of sample A (dark blue line) and its passivated - sample AH. (b) The Projected DOS of one sample A (unpassivated) and AH (passivated). Fermi levels is set to zero. The inset on lower window indicate the zooming of CBM edges.

Figure 5. (Color online) Spatial distribution of HOMO and LUMO states of unpassivated sample A (top row) and passivated sample AH (bottom row). In this figure, galium and nitrogen atoms are shown in bedge and dark blue colors, respectively.
5. Band-related transport properties

From this analytical representation of NW’s band structure we calculate the derivatives necessary for the transport distributions. Based on the carefully calculated 1D bandstructure of SL NW along wire growth direction $z$, we have attempted to estimate the electrical conductivity $\sigma$ and the Seebeck coefficient (also known as thermo-power) $S$ and electronic contribution to the thermal conductivity $\kappa_0$ through the semiclassical Boltzmann’s transport theory within the constant relaxation time approximation, as implemented in the BoltzTraP code [29]. This implementation relies on the smoothed Fourier expansion of the band’s energies, provided by first-principles electronic structure calculation, i.e. by Siesta code at the above section. For the detail of the calculation we address to the similar scheme what was done in [30] for SrTiO$_3$/SrRuO$_3$ superlattices. As the group velocity is estimated from the first-principles calculations as a numerical derivative of band energies in a numerical mesh for the Brillouin zone sampling, there requires very fine grid. Since NW structures have only one infinite periodical dimensions of $z$, i.e. wire growth direction, so that only $zz$ tensor component of transport properties are of interest. Fig.6a shows the temperature dependence of $ZZ$-component of tensor electrical conductivity per relaxation time $\sigma_{zz}/\tau$ of studied structure. All structures show similar behaviour but the unpassivated (solid lines) and passivated (dashed lines) are different in 20 times in scaled showing the negative influence of surface confined states into conductivity and mobilities along wire. Similar tendency is also observed for $ZZ$-component of electronic thermal conductivity tensor $\kappa_0$ (Fig6.2) showing that the thermal conductivity is also affected by surface reconstruction and surface confined states. Finally the Seebeck coefficient tensor $S_{zz}$ of unpassivated wire have a sharp peak at low temperature before slowly monotonic increase as for the passivated case (see Fig.6.c).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{(Color online) (a) ZZ-component of electrical conductivity tensors $\sigma_{zz}/\tau$ as a function of relaxation time $\tau$ and temperature $T$ (b) ZZ-component of electronic thermal conductivity tensor $\kappa_0$ vs $T$ (c) ZZ-component of Seebeck coefficient tensor $S_{zz}$ vs $T$.}
\end{figure}

6. Conclusions

We have presented in this work a study on the role of the surface reconstruction in several structures representing the GaN SL hetero-crystal-phase NWs with different size and composition. The effects of the surface reconstruction is estimated by the passivated NW model in which the dangling bonds on the NW’s surface are saturated by fractionally charged pseudo hydrogen atoms. We have found that in this passivated NW model, as expected, effects from the surface reconstruction on the structural and electronic properties of the NWs are almost suppressed, leaving just a quantum confinement size effect. The structural and electronic properties of the NWs, i.e. Band and DOS, are strongly affected by the surface reconstruction. In particular, the band structure of the NWs is dramatically changed because of the surface reconstruction as there introduced a large number of in-gap states right in the vicinity of the VBM and the CBM. The WZ-Zb interface form a type II quantum well and serves as charge separation for the excitonic pair and help to enhance the optical properties of SL NWs. The
calculated transport properties of these SL NWS have also been strongly affected by the present of the in-gap surface states.

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