First-Principles Investigations of Intrinsic and Si-doped GaAs Nanowires: Structural Stability and Electronic Properties

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Abstract. High quality GaAs nanowires (NWs) are nowadays experimentally grown on different substrates, regularly shaped and nicely oriented. At variance with the bulk phase, they show a prevalence of wurtzite structure with respect to zincblende and a p-type behavior with respect to the possible amphoteric behavior upon Si incorporation. Motivated by these recent experimental findings we investigate by first principles pseudopotential calculations the structural stability and electronic properties of GaAs NWs. The nature of Si dopants in GaAs NWs and the relative stability of donors and acceptors have been also studied. Our results show that wurtzite NWs are more stable than zincblende NWs for diameters of 50 Angstrom or less. On the basis of the formation energy only, Si dopants have amphoteric behaviour in GaAs NWs and segregates at the surface of the wire.

Keywords: Semiconductors, Nanowires; GaAs; zincblende; wurtzite; Density Functional Theory; First-principles Pseudopotentials; Donors; Acceptors
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INTRODUCTION

Semiconductor nanowires (NWs) offer nowadays new perspectives for nano-electronic devices. Recently, high quality GaAs NWs have been experimentally grown on different substrates: they are regularly shaped and nicely oriented, with wurzite (WZ) or zincblende (ZB) structure depending on the substrate and on the growth conditions [1]. It is well known that Si has amphoteric behaviour in bulk; in NWs, at variance, mainly p-type doping is observed upon Si incorporation.

The main issues of the present work are therefore to understand by means of accurate first-principles total energy and electronic structure calculations why NWs are observed also in WZ structure and why the behaviour of Si dopants in NWs is different with respect to the bulk.

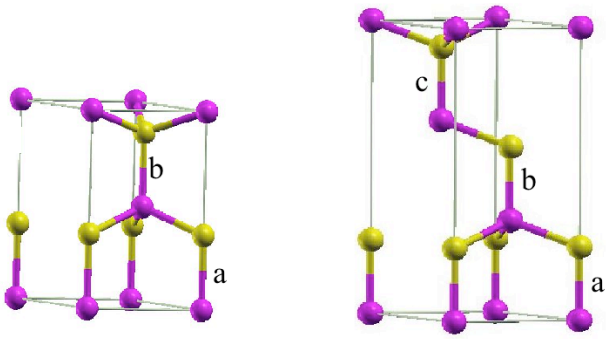

FIGURE 1. Stacking of WZ and ZB structures along (0001) and (111) directions respectively; a,b,c indicate the non equivalent anion-cation double layers.

NUMERICAL APPROACH

Calculations have been performed within the framework of Density Functional Theory in the local density approximation using first-principles pseudopotentials to describe the valence electrons and plane wave as a basis set to expand the electronic wavefunctions. Periodically repeated supercells are used for a convenient reciprocal space formulation of the problem. The Quantum-Espresso package has been used [2].

The relative stability of bulk ZB phase of GaAs is correctly described by our numerical simulations, that give a difference in the cohesive energy between ZB and WZ phase of ~11 meV/atom, in good agreement with the literature. It is meaningful to compare ZB and WZ structures along (111) and (0001) directions respectively, where they are similar but with a different stacking of anion-cation double layers: the stacking sequence for ZB is *abcabc*... and for WZ is *ababab*... (Fig. 1).

A NW is characterized by its structure (ZB or WZ), its shape around the growth axis (Triangular (T) or Hexagonal (H)) and the number of atoms in each double layer ((n_a,n_b,n_c) for ZB and (n_a,n_b) for WZ) (Fig. 2). In all cases the exposed facets are non – polar, containing the same number of Ga and As atoms.

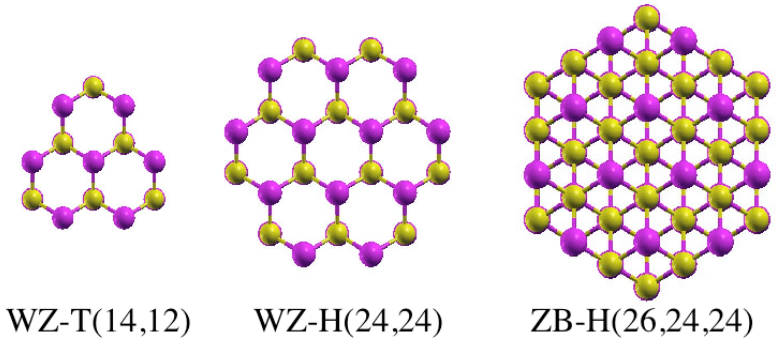

FIGURE 2. Projected section view of some NWs with different shape and size.

RESULTS

Undoped GaAs Nanowires

We have studied the cohesive energy of WZ-H, WZ-T and ZB-H GaAs NWs. We have performed full supercell calculations for NWs with diameter up to about 20 Angstrom, corresponding to the structure WZ-H(54,54). We have calculated the cohesive energy as:

$$E_c = \left\{ \sum_i n_i \mu_i - E_{tot} \right\} / \sum_i n_i$$

where E_{tot} is the total energy of the supercell containing the GaAs NW, μ_i is the chemical potential of atoms *i* (*i*=Ga or As) and n_i is the number of *i* atoms.
Similarly to findings reported in Ref. [3] for InP NWs, GaAs NWs are more stable in WZ than in ZB structure for diameters smaller than 20 Angstrom.

The stability is mainly determined by the dangling bonds (DB) at the NWs facets: in WZ NWs 3-fold coordinated atoms are present (we refer to them as DB_1), whereas in ZB NWs also 2-fold coordinated atoms (DB_2) are present.

Following Ref. [3], we can express the NWs cohesive energy in terms DBs contributions:

$$E_c^{NW}(WZ) = E_c^{bulk}(WZ) - \frac{N_{DB}^1}{N_{tot}} E_{DB}^1 \quad , E_c^{NW}(ZB) = E_c^{bulk}(ZB) - \frac{N_{DB}^1}{N_{tot}} E_{DB}^1 - \frac{N_{DB}^2}{N_{tot}} E_{DB}^2$$

where $E_c^{(bulk\ ZB)}$ is the cohesive energy of the bulk ZB (similarly for WZ), $E^{(1)}_{DB}$ and $E^{(2)}_{DB}$ are the energy contributions of 3-fold and 2-fold coordinated atoms respectively and $N^{(1)}_{DB}$ and $N^{(2)}_{DB}$ their number in the NW. Fitting data obtained from full supercell NWs calculations it is possible to estimate $E^{(1)}_{DB}$ and $E^{(2)}_{DB}$, that can be used in the previous Equation to find the cohesive energy for ZB and WZ NWs with larger diameter. We obtain: $E^{(1)}_{DB}(WZ)$=0.54 eV, $E^{(1)}_{DB}(ZB)$=0.48 eV, $E^{(2)}_{DB}(ZB)$=1.17 eV.
On the basis of these values, we estimate that undoped WZ NWs are more stable than ZB NWs up to a diameter of at least 50 Angstrom; for larger diameters (between ~50 and 100 Angstrom) the two NW structures become energetically equivalent within the numerical accuracy of the cohesive energy; for even larger diameters the DB contribution reduces with respect to the volume, going towards the limit of the two corresponding bulk structures with ZB slightly favoured with respect to WZ.

We point out that, in spite of the presence of surface DB, GaAs NWs are semiconducting. Surface relaxations (As move outwards, Ga inwards) act in the direction of compensating DBs.

Si doped GaAs Nanowires

It is well known that Si atoms have amphoteric behaviour in bulk GaAs, substituting both Ga and As atoms. However, donors are typically favoured in

Molecular Beam Expitaxy growth conditions. We have calculated the formation energy of neutral Si donors and acceptors in both ZB and WZ bulk GaAs matrices using 32-atoms supercells with one Si atom substituting one Ga or one As respectively. Our results are in agreement with findings in Ref. [4]: the formation energies for Si donors and acceptors with respect to Si chemical potential are:

$$\Delta\Omega_d^{ZB}(\Delta\mu,\mu_{Si}) = 1.46eV + \frac{\Delta\mu}{2} - (\mu_{Si} - \mu_{Si}(bulk))$$

$$\Delta\Omega_a^{ZB}(\Delta\mu,\mu_{Si}) = 1.27eV - \frac{\Delta\mu}{2} - (\mu_{Si} - \mu_{Si}(bulk))$$

$$\Delta\Omega_d^{WZ}(\Delta\mu,\mu_{Si}) = 1.58eV + \frac{\Delta\mu}{2} - (\mu_{Si} - \mu_{Si}(bulk))$$

$$\Delta\Omega_a^{WZ}(\Delta\mu,\mu_{Si}) = 1.39eV - \frac{\Delta\mu}{2} - (\mu_{Si} - \mu_{Si}(bulk))$$

($\Delta\mu$ is the difference between the chemical potentials of Ga and As).

The formation energy of Si dopants in NWs depends on intrinsic characteristics of the host NW (structure, shape and diameter) and on the particular substitutional site, which can vary from a bulk-like position close to the center of the NW to different non-equivalent surface positions (middle of facets, close to edges, fully 4-fold or 3-fold or 2-fold coordinated sites). As a general trend, we found that dopants are more stable on the facets of the NWs. Concerning the relative stability of donors with respect to acceptors, the trend is similar to the bulk case: Si donors are favoured with respect to acceptors. Detailed results will be presented in a future work.

CONCLUSIONS

Undoped GaAs NWs are stabilized for small diameter in WZ rather than in ZB structure. The possibility of bistability for larger diameters is consistent with the experimental observations, depending on the growth mechanism. Similarly to bulk, Si is found to have an amphoteric behaviour also in the NWs, based on energetics only. The experimental observation of p-type behavior mainly of Si-doped NWs could be due to the kinetics of Si incorporation.

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