Ab-initio investigation of point-like defects in AlN nanowires

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Abstract. We have studied the relaxed atomic configurations and formation energies of intrinsic and some extrinsic point-like defects in atomic-sized wurtzite AlN wires, by means of density-functional calculations, using local basis sets. The results indicate that the most likely native defects in small AlN nanowires are interstitial N atoms, while in the case of doping with Si, the impurity is most likely to substitute an Al atom.

1. Introduction
It is well known that structures at the nanometer scale exhibit peculiar effects that make them interesting candidates for future quantum information technology \([1]\), UV \([2]\) and field emitters \([3]\) or chemical \([4]\) \([5]\) and temperature sensors. The fabrication of quantum gates and qubit manipulation is an essential part for such technology. Recently, single molecule, atomic chain and break-junction devices have attracted a great deal of interest, from both experimental and theoretical point of view. As such, mechanically controlled break-junction techniques are used for producing mono-atomic chains. Unlike their bulk counterparts, the influence of structural point-like defects on the physical properties of nanostructured systems is much less known, both from the experimental and theoretical point of view. The changes in the conduction properties produced by some intrinsic or extrinsic defects which are likely to appear in structures such as nanowires with a cross section of one or more lattice constants were addressed in \([6, 7]\). Since the results in \([7]\) show that the transport properties are drastically influenced by the presence of impurities, a more detailed study of defects in AlN nanowires is considered in the present work. Up to this point, most theoretical studies have either investigated defects in bulk AlN \([8]\), surface defects in AlN nanowires \([9]\) or point defects in single walled AlN nanotubes \([10]\), but very few have been focused on the study of point defects in AlN nanowires.

In this study we investigate atomic configurations and formation energies of small-diameter AlN nanowires containing native defects (cation and anion vacancies and interstitials) and Si impurities using \textit{ab-initio} density-functional calculations.

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2. Calculation Method

Atomic-sized wurtzite AlN nanowires with longitudinal axis along the [001] direction were investigated. All calculations were based on the density-functional theory (DFT) method, in the approach implemented in the SIESTA method [11], with the exchange-correlation term parametrized as proposed by Ceperley and Alder [12]. The wavefunctions were expanded using a localized double-$\zeta$ polarized basis set; such localized basis orbitals allow to achieve a linear scaling of the computational time with the number of atoms involved. The Monkhorst-Pack [13] scheme with \((1 \times 1 \times 5)\) mesh points in \(k\)-space was used to perform integrations over the Brillouin zone.

A super-cell containing six pairs of Al-N atomic layers (equivalent to three unit cells along [001] crystalline direction) was used, with sufficient vacuum space in the two transverse directions (60.2 Å by 60.2 Å) to avoid interaction between wires in adjacent cells. While considering as initial input the experimental values for the wurtzite bulk lattice constants, \(a_{\text{AlN}} = 3.112\) Å, \(c_{\text{AlN}} = 4.982\) Å, a structural relaxation was performed until the inter-atomic forces were less than 0.01 eV/Å. For all considered neutral point-like defects, the formation energy was calculated as in [19]:

\[
E_f(X, q) = E_{\text{def}}^{\text{tot}} - E_{\text{perf}}^{\text{tot}} - n_A\mu_A - n_N\mu_N - n_X\mu_X, \tag{1}
\]

where \(E_{\text{def}}^{\text{tot}}\) is the total energy of the relaxed, defected nanowire, \(E_{\text{perf}}^{\text{tot}}\) is the total energy of the nanowire without defects, \(\mu_A\), \(\mu_N\) and \(\mu_X\) are the chemical potentials of Al,N and impurity X, and \(n_A\), \(n_N\) and \(n_X\) are the number of exchanged particles between the super-cell and the reservoir; \(n > 0\) if atoms are added to the nanowire and \(n < 0\) if atoms are removed from it. Another important parameter used when computing the formation energy is the chemical potential reference. The results presented here were obtained for both technologically limited conditions: the case of a nitrogen rich or that of an aluminum rich growth environment. As indicated in [19], the upper bounds for the chemical potential are given by: \(\mu_A \leq \mu_A^{\text{bulk}}\) and \(\mu_N \leq \mu_N^{\text{bulk}}\). The reason for choosing as reference the chemical potential of solid nitrogen is because these calculations were carried out for 0 K, where AlN, Al and N are found in their solid phase. The lower bounds of the chemical potential are given by:

\[
\mu_A + \mu_N = E_{\text{AlN}}^{\text{tot}} \tag{2}
\]

where \(E_{\text{AlN}}^{\text{tot}}\) is the total energy for a Al-N pair in the defect-free nanowire and \(\mu_A\) or \(\mu_N\) are found by fixing either one at a time. The bulk chemical potentials for N is \(\mu_N^{\text{bulk}} = -269.80\) eV and for Al, \(\mu_A^{\text{bulk}} = -56.97\) eV. In the case of Si defects, the chosen reference chemical potential is that of bulk silicon (\(\mu_{\text{Si}}^{\text{bulk}} = -160.26\) eV) because the main chemical component that can form in the presence of Si is silicon nitride which has a molar enthalpy of formation of 829 kJ, according to [20], being more than double that of aluminum nitride (320 kJ [21]).

3. Results and discussions

As previously observed for boron nitride in [14], the perfect R 1 relaxed nanowire is of graphite-like type (Fig. 1 - images obtained with xcrysden [15]); the Al-N bonds lengths are indicated in Table 1. The R 1 nanowire can also exist in a collapsed, graphite-like phase (Fig. 1) with bond lengths also indicated in Table 1. An important piece of information is that the collapsed R 1 nanowire has a slightly more stable structure than the cylindrical one, having an energy lower by 0.02 eV per Al-N pair. In order to determine if the increased stability of the collapsed phase is valid for larger radii, a single walled nanotube with 40 atoms/super-cell was also investigated. The collapsed nanotube, which is basically a two layer AlN ribbon, has an energy 0.15 eV lower
Table 1. Bond lengths in the defect-free nanowires

| Bond between atoms          | Bond length (Å) |
|-----------------------------|-----------------|
| **R 1 nanowire**            |                 |
| in the transversal plane    | 1.97            |
| along the [001] direction   | 1.88            |
| **collapsed R 1 nanowire**  |                 |
| in the transversal plane    | 2.03            |
| along the [001] direction   | 1.88            |
| **R 2 nanowire**            |                 |
| in the transversal plane    |                 |
| 1-2                         | 1.82            |
| 2-3                         | 1.87            |
| 3-4                         | 1.99            |
| along the [001] direction   |                 |
| 1                           | 1.79            |
| 2                           | 1.79            |
| 3                           | 1.94            |
| 4                           | 1.95            |
| **R 3 nanowire**            |                 |
| in the transversal plane    |                 |
| a-1                         | 1.80            |
| 1-2                         | 1.87            |
| 2-3                         | 2.00            |
| 3-b                         | 1.92            |
| along the [001] direction   |                 |
| 1                           | 1.78            |
| 2                           | 1.92            |
| 3                           | 1.95            |

per Al-N pair than the cylindrical one, indicating a result which is in agreement with the ones presented in [16], [17] and [18] for carbon nanotubes. The bond lengths of the defect-free $R_2$ nanowire (Fig. 2) and the defect-free $R_3$ nanowire (Fig. 1) are also indicated in Table 1.

Because the nanowire has a broken translational symmetry in the transversal plane, Al and N vacancies have more nonequivalent locations than in the bulk material, as can be seen in Fig. 1 for the $R_1$ nanowire (in both cylindrical and collapsed phase) and the $R_3$ nanowire, and in Fig. 2 for the $R_2$ nanowire. When indicated by "center" it means that in the relaxed configuration the impurity resides in the interior of the nanowire and if no indication is given, the impurity is found in the plane or on the exterior surface of the nanowire, forming bonds with atoms of the nanowire wall.

It is worth mentioning that the collapsed $R_1$ nanowire with an interstitial Al atom reaches a single relaxed configuration, independent on the initial positions, with the Al atom forming a 1.97 Å bond with an N atom, and a $134.6^\circ$ angle with both walls of the nanowire. On the other hand, the N interstitial can be found in three relaxed final configurations, forming
distorted bonds on either one of the different nanowire walls, or inside in its interior.

An interesting result is also obtained for an Al vacancy in position 1 (Fig. 2) of the $R_2$ nanowire because only for this type of defect the system relaxes into a graphite-like structure (Fig. 2), similar to the one found for $R_1$. The cell suffers a contraction by 25.9% along the nanowire axis from 5.09 Å to 3.77 Å. Since the defected graphite-like phase is more energetically stable than the defect-free nanowire, the formation energy for the Al vacancy in position 1 is negative for both N (-11.51 eV) and Al (-10.31 eV) rich growth conditions. This means that nanowires of this type are very unlikely to exist, especially in the wurtzite phase, since Al vacancies have a natural tendency to appear.

The formation energies of the defects described above were computed in the case of a neutral charge, in both N and Al rich environments. From the defect formation energy it can be seen that in the case of the $R_1$ nanowire (Table 2 and Fig. 3) interstitial N is the most probable intrinsic defect in the N rich limit, while interstitial Al is the most probable in the case of an Al rich growth environment. In the case of Si doping, the most probable defect is a substitution of Al.

In the case of the collapsed $R_1$ nanowire (Table 3 and Fig. 4), the most probable intrinsic defect is interstitial N in the N rich condition, and interstitial Al for the Al rich environment, while Si substitutes Al the easiest.

For the $R_2$ nanowire, the Al vacancy that leads to the graphite-like phase has a decisive role and indicates an unstable structure. As such, the subsequent calculations for the formation energies of other defects were not included.

The largest diameter nanowire, $R_3$ (Table 4 and Fig. 5), is most likely to contain interstitial Al in both N rich and Al rich conditions. Also, in this case, a Si impurity is most likely to appear as a substitutional defect of Al in both N and Al rich conditions.

**Figure 1.** Relaxed R 1, R 1-collapsed and R 3 nanowires (where indexes a and b are only used to indicate bond lengths)
Figure 2. Relaxed R 2 nanowire

Figure 3. Intrinsic defect formation energies for the R 1 nanowire

| Defect type                  | $E_f$ (eV) - N rich | $E_f$ (eV) - Al rich |
|------------------------------|--------------------|---------------------|
| Si interstitial              | 2.61               | 2.61                |
| Si interstitial (center)     | 9.26               | 9.26                |
| Si substitutional (Al)       | 1.108              | 2.31                |
| Si substitutional (N)        | 4.39               | 3.19                |

Table 2. Extrinsic defect formation energies for the R 1 nanowire

4. Conclusions
The relaxed configurations and formation energies of selected defect were obtained for four types of AlN nanowires. It was found that single walled nanotubes can also be found in a more energetically favorable collapsed configuration. An indication for the instability of $R$ 2 type
Defect formation energy (eV)

$\mu$

Figure 4. Intrinsic defect formation energies for the R 1 collapsed nanowire

Defect formation energy (eV)

$\mu$

Figure 5. Intrinsic defect formation energies for the R 3 nanowire

| Defect type            | $E_f$ (eV) - N rich | $E_f$ (eV) - Al rich |
|------------------------|---------------------|---------------------|
| Si interstitial        | 2.69                | 2.69                |
| Si interstitial (center)| 3.64               | 3.64               |
| Si substitutional Al (1)| 1.69               | 2.89               |
| Si substitutional Al (2)| 1.28               | 2.48               |
| Si substitutional N (1)| 4.02                | 2.82               |
| Si substitutional N (2)| 5.31                | 4.11               |

Table 3. Extrinsic defect formation energies for the collapsed R 1 nanowire
Defect type & $E_f$(eV) - N rich & $E_f$ (eV) - Al rich \\
Si interstitial & 1.80 & 1.80 \\
Si interstitial (center) & 9.86 & 9.86 \\
Si substitutional Al (1) & 0.17 & 1.37 \\
Si substitutional Al (2) & 0.71 & 1.91 \\
Si substitutional Al (3) & 1.03 & 2.23 \\
Si substitutional N (1) & 5.98 & 4.78 \\
Si substitutional N (2) & 4.08 & 2.88 \\
Si substitutional N (3) & 6.71 & 5.51 \\

Table 4. Extrinsic defect formation energies for the R 3 nanowire

nanowires is given by the negative formation energy of Al vacancies. The formation energies indicate the most probable intrinsic defect to appear in R 1 nanowires is that of interstitial N, in N rich environment, and interstitial Al in the Al rich environment, while in the case of R 3 nanowires interstitial Al is most probable. For all the nanowires studied in this paper Si atoms will most easily substitute Al.

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