Theoretical simulations of regular and defective aluminium nitride nanotubes

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Abstract. For theoretical simulation on AlN nanotubes (NTs) of different chiralities (armchair- and zigzag-type) and uniform diameters, we have considered their single-walled (SW) 1D periodic models. For this aim, we have performed \textit{ab initio} DFT calculations on AlN SW NTs using formalism of the localized Gaussian-type atomic functions as implemented in \textit{CRYSTAL-03} computer code. We have shown that the smaller the diameter of AlN single-walled nanotube is, the closer its electronic and structural properties to AlN bulk. We have analysed an influence of N vacancies (neutral F centres) created by either soft irradiation of nanotubes or under experimental conditions of their growth, on the atomic and electronic structure of AlN SW NTs. We have found the small inward relaxation of the Al nearest neighbours and the N next-nearest neighbours around each point defect formed on 1 nm AlN NTs of both chiralities. Presence of N vacancy in both types of nanotubes has resulted in appearance of the two defect energy levels in their band gaps consisting of mainly $3s$ and $3p$ states of the nearest Al atoms.

1. Introduction

Due to numerous technological applications, AlN nanostructures attract enhanced attention of both experimentalists and theorists [1-5], for instance, AlN in GaN-based nanoelectronics [6]. Different AlN nanotubes (NTs) of a wide range of diameters (up to 80 nm) were recently synthesized using either a method of highly non-equilibrium direct current (DC) arc-plasma-induced melting of aluminium in N-Ar ambient [2] or simply nitriding impregnated Al powder in a tubular furnace [3]. In both cases, nanotubes identified using high-resolution transmission electron microscopy (HRTEM) were accompanied by nanoclusters and nanowires. AlN nanosystems containing both nanotubes and nanoparticles have been recently studied experimentally [7] using spectroscopic methods of XANES (X-Ray absorption near edge spectroscopy), FTIR (Fourier transform infra-red spectroscopy) and XAS (X-ray absorption spectroscopy), all sensitive to the local order of nanostructures and correlated to the density of their electron states, as well as X-ray diffraction (XRD) which can detect the subtle
structural modifications of nanosamples. The time-of-flight (TOF) data obtained for neutron scattering on AlN NTs [8] are linked to their vibrational density of states depending on the distribution of phonon frequencies. Actually, experimentally synthesized NTs are rather smooth nanorods with hollow centres and comparatively thick walls, which were found to be characterized by Al and N atom arrangements according to either hexagonal \textit{wurtzite} structure as in a stable $w$-AlN bulk [3,4,7] or cubic \textit{zinc-blende} structure as in metastable $zb$-AlN bulk [2,7]. Diameters of these nanotubes with averaged length $\sim 700$ nm were identified to be either small, 2-4 nm, or large, 20-80 nm [2,3,7], whereas thickness of their walls were estimated to be from 1 up to 20 nm [3]. Unlike boron nitride NTs synthesized earlier, which possess graphitic and honeycomb network on the tube single walls (SW) [9], no experimental observation of similar SW structures in AlN, GaN and InN has been reported so far. Probably this difference arises due to existence of honeycomb nanosheet structures at both BN and carbon graphitic surfaces, which can be rolled up in single-walled nanotubes whereas in other III group nitrides they are rather metastable or unstable.

Meanwhile, most theoretical simulations on AlN NTs performed so far used a smooth cylindrical SW model [4,5,10-14], \textit{i.e.}, the simplest \textit{1D} nanostructure characterized by either armchair- or zigzag-type chiralities (Fig. 1) and wide range of uniform diameters (0.5-6 nm). Due to $sp^3$ hybridisation of metal-nitrogen bonds, these graphitic-like layered tubular structures were found to be energetically stable. For their theoretical simulation, both finite cage-like clusters [4,5,11] and periodic DFT-LCAO calculations confirm the former; (iii) in ab initio calculations, this value becomes larger: 12.5-13.0 eV [10]; (iv) using the force-field conjugate gradient algorithm combined with \textit{ab initio} calculations [13], a thermal stability of the AlN NTs was simulated: it was shown that SW NTs can stably exist at room temperature ($T \sim 300$ K) and melt at $T > 600$ K.

The first theoretical paper, which considers a multi-walled (MW) AlN NT, has been just published [16]. It was found that too high strain energy of an AlN honeycomb nanosheet structure relative to stable $w$-AlN bulk structure, as a main reason of instability for AlN SW NT, can be reduced by consequent growth of nanotube wall thickness through nanorod to nanowire which internal structure is close to \textit{wurtzite} and shape of cross section is similar to a quasi-hexagon. For this type of nanostructure (nanowire), the larger the diameter is, the closer its properties to bulk.

Obviously, experimental conditions of AlN nanotube growth [2,3] unavoidably lead to appearance of point defects, such as vacancies, antisites or substitutional impurities as considered in the first DFT-PW study devoted to theoretical simulation of defective AlN NTs [17]. Presence of intrinsic defects affects both electronic and mechanical properties of NTs; they are also chemically active sites for nanotube wall functionalisation. In our latest study on AlN NTs containing N vacancies [18] we have shown that the larger the content of N vacancies in nanotube is, the closer its electronic structure to an AlN \textit{n}-type surface [10], with substantially smaller gap between the nearest energy levels as compared to defectless AlN bulk or AlN NT of small diameters. The dangling bond saturation around N vacancy can be achieved by Al$_N$ antisite as well as C$_N$ and O$_N$ substitutes [17]. The Al atom as a substitute for N in the AlN NTs was found to be out of the tube by 1.5 Å and does not result in occurrence of local metallic behaviour. Both C$_N$ and O$_N$ substitutes do not introduce strong lattice deformations since they are structurally similar to missing N atom. Presence of O$_N$ impurities in AlN NT leads to a local metallicity since the Fermi level crosses a defect band in the gap [17] whereas C$_N$ defect simply introduces defect electronic states in AlN NT band gap, similarly to a N vacancy.
In this paper, we analyse and verify results of our recent DFT-LCAO calculations on structural and electronic properties of periodic AlN SW NTs of different chiralities (armchair- and zigzag-type) and uniform diameters (1 and 6 nm), both defectless [10] and containing neutral N vacancies (F centres) of different concentration [18]. We clarify the influence of N vacancies on properties of defective AlN NTs as compared to those we have obtained for defectless nanotubes. We also compare calculated properties with available experimental and theoretical data for AlN nanotubes of both chiralities, (0001) n-type surface and bulk (both w-AlN and zb-AlN).

2. Theoretical background

2.1. Computational details

Periodic DFT calculations on six 1D models of regular and defective single-walled AlN nanotubes (Figs. 1-3) have been performed using the LCAO formalism of localized Gaussian-type functions (GTFs) as implemented in the CRYSTAL-03 code [19]. For this aim, we have used the non-local PWGGA (Perdew-Wang Generalized Gradient Approximation) exchange-correlation functional [20]. The all-valence basis sets for Al and N GTFs (8s-511sp-1d and 81s-31p-1d, respectively) were optimized elsewhere (for several Al-containing compounds [21] and GaN [22]), we have only slightly re-optimized their valence and virtual shells. The reciprocal space integration has been performed using the suitable shrinking factors for the Monkhorst-Pack and Gilat nets: 4 × 4 × 8 [23,24]. To simulate the F centres, N atoms from AlN SW NTs of both chiralities were removed (Fig. 3), retaining in the vacancy the wave function of the missing ion (the so-called ghost basis set [19]).

2.2. 1D models of AlN SW NTs

Models of regular 1 nm and 6 nm armchair-type AlN NTs are considered as (n,n) periodic structures (rod symmetry Pn/m) which include 24 and 144 atoms in the corresponding 1D unit cells (6,6) (Fig. 1a) and (36,36) (Fig. 2a). For the 1 nm- and 6 nm-zigzag-type AlN NTs (rod symmetry Pnmm), we construct (10,0) (Fig. 1b) and (64,0) (Fig. 2b) unit cells which include 40 and 256 atoms, respectively. For all the AlN NTs models, we have optimised the length of the nearest AlN bond, which results in the changes of the corresponding nanotube diameters as well.

Figure 1 (Color online). Fragments of 1 nm thick AlN nanotubes with a) armchair-type and b) zigzag-type chiralities. For better distinction between both chiralities, gray (light) and brown (semi-dark) balls correspond to Al atoms of the former and latter morphology, respectively, whereas N atoms are shown as blue (dark) balls.

Symmetry of 1 nm thick armchair- and zigzag-type AlN SW NTs (Fig. 3) containing single N vacancies is practically broken as compared to the corresponding defectless nanotubes shown in Fig. 1. For the defective armchair-type nanotube, rod symmetry of their cross-section plane is reduced to Pm (Fig. 3a) whereas for zigzag-type NT, no symmetry operators exist, i.e., its rod symmetry is P1.

For simulation of defective 1 nm thick AlN NTs, we have fixed the optimised AlN bond lengths of the corresponding defectless nanotubes (Table 1) with further removal of N atom per one supercell and relaxation of three circles of atoms nearest to the newly-formed F centre [18]. Thus, calculations on defective AlN NTs is much more space- and time-consuming as compared to those on perfect AlN nanotubes [10]. To approach a single vacancy limit for both nanotube chiralities, we have considered
three sets of inter-defect distances repeated along the axes of these nanotubes: 13.5, 20.25 and 27.0 Å for armchair-type NT (Fig. 3a) as well as 10.8, 21.6 and 32.4 Å for zigzag-type chirality (Fig. 3b).

3. Results and discussion

In this paper, we analyse calculated properties of AlN SW NTs as presented in Table 1 (for perfect nanotubes: equilibrium bond length $r_{\text{min}}(\text{Al-N})$, binding energy $E_{\text{bind}}$ per Al-N bond, effective charges $q_{\text{Al}}$ and $|q_{\text{N}}|$, energy band gap $\Delta \varepsilon_{\text{gap}}$) and Table 2 (for defective nanotubes: relaxations of first and second atomic circles around $F$ centre $r_{F,\text{Al}}$ and $r_{F,\text{N}}$, charge induced on $F$ centre $\Delta q_{F}$, defect formation energy $E_{\text{form}}(F)$ and largest defect gap $\Delta \varepsilon_{\text{max}}$ inside the band gap of perfect nanotube), comparing them with the corresponding properties of AlN bulk and surface as well as data available from literature. We also present band structures of perfect and defective 1 nm thick AlN NTs (Figs. 4, 5, respectively).

3.1. Perfect AlN NTs. According to our results presented in Table 1, the larger is an AlN NT diameter, the closer values of $E_{\text{bind}}$, $q_{\text{Al}}$ ($|q_{\text{N}}|$) and $\Delta \varepsilon_{\text{gap}}$ to those obtained for the densely-packed surfaces with hexagonal structure, at least, they slightly decrease, being rather averaged between the corresponding values for AlN bulk and graphitic or honeycomb sheet. Qualitatively, values presented in Table 1 correspond to those obtained in various theoretical and experimental studies. This trend is also confirmed by analysis of rolling up sheet-to-cylinder strain energy: it noticeably reduces with increase of NT diameter [14]. As to qualitative difference with slight asymptotic increase of $\Delta \varepsilon_{\text{gap}}$ for the larger AlN NTs observed earlier [12], in that study calculations were performed for nanotubes with
diameters up to 1.5-2.0 nm only, which are too thin to observe any approach to the surface or sheet properties. Moreover, DFT-PW calculations on band gaps performed for AlN crystals and nanotubes noticeably underestimated $\Delta \varepsilon_{\text{gap}} [4,12,13]$, although in our calculations, band gap for $w$-AlN bulk is overestimated by ~1.2 eV [10] as compared to experimental value of 6.2 eV [15]. As a result of this difference, disagreement in description of dependence of $\Delta \varepsilon_{\text{gap}}$ on NT diameter can be also possible.

### Table 1. Structural and electronic properties calculated for the 3D, 2D, 1D models of AlN

| Properties $^a$ | Source | Bulk | AlN surface $^b$ | Single-walled NT (Figs. 1,2) |
|-----------------|--------|------|------------------|-----------------------------|
| $r_{\text{min}}$(Al-N), Å | our data $^{[10]}$ | 1.86 | 1.84 | 1.84 | 1.79 | 1.79 | 1.80 | 1.80 |
| | reference | 1.89$^{[15]}$ | 1.90$^{[13]}$ | – | 1.77$^{[11]}$ | 1.83$^{[12]}$ |
| $E_{\text{bind}}$(Al-N), eV | our data $^{[10]}$ | 14.37 | 14.26 | 11.51 | 11.41 | 12.80 | 12.79 | 12.67 | 12.66 |
| | reference | 16.0$^{[13]}$ | – | – | 9.0$^{[11]}$ | 10-11$^{[11]}$ |
| $q_{\text{Al}}$ and $|q_{\text{N}}|$, e $^c$ | our data $^{[10]}$ | 2.27 | 2.22 | 2.20 | 2.19 | 2.26 | 2.26 | 2.23 | 2.22 |
| | reference | – | – | – | 2.55$^{[11]}$ |
| $\Delta \varepsilon_{\text{gap}}$, eV | our data $^{[10]}$ | 7.4 | 7.2 | 2.5 | 2.1 | 7.1 | 6.9 | 6.8 | 6.6 |
| | reference $^d$ | 6.2$^{[15]}$ | 5.2-5.7$^{[25]}$ | < 2$^{[26]}$ | 4.8-5.6$^{[11]}$ |

$^a$ description is given at the beginning of Section 3

$^b$ the corresponding values are averaged across the slab;

$^c$ note that AlN molecule is substantially more covalent compound: $q_{\text{Al}} = +1.5$ e and $q_{\text{N}} = -1.5$ e.

$^d$ we have not included here results of several DFT-PW calculations underestimated $\Delta \varepsilon_{\text{gap}}$ by >1 eV.

![Figure 4](image-url)

**Figure 4.** Two band structures of defectless 1 nm thick AlN SW nanotubes per unit cells possessing either armchair-type (a) or zigzag-type (b) chirality.

Band structures of perfect AlN nanotubes shown in Fig. 4 clearly illustrate difference in electronic structure of both chiralities: if zigzag-type NTs possess a direct band gap which means that such nanostructures may exhibit strong electro-luminescence never observed in the bulk materials [15] then armchair-type NTs have an indirect band gap (values of $\Delta \varepsilon_{\text{gap}}$ are present in Table 1). In both cases, the upper areas of valence bands (VB) are characterized by superposition of N(2p) and Al(3p) states, with smaller contribution of Al(3s), whereas the lowest conduction bands (CB) are predominantly Al(3s).
3.2. AlN NTs containing N vacancies. Atom relaxations around a single $F$ centre for both chiralities of AlN SW NTs (Fig. 3) are found to be larger than in AlN bulk and graphitic sheet (Table 2): the three nearest Al neighbours of an N vacancy are shifted by 0.22-0.23 Å from their lattice sites towards the defect and inside the nanotube whereas the next-nearest N atoms are relaxed in the same directions more weakly (0.07-0.08 Å) [18]. Relaxation of atoms nearest to N vacancy in AlN nanotube is much stronger than that in AlN bulk and surface (both phases). These results confirm conclusions drawn is recent study of defective CNT [27]: the main reason of larger atomic relaxation in nanotubes is found to be the strained NT structure as compared to bulk and surface. The electronic charges induced on $F$ centres with relaxed structure of armchair- and zigzag-type AlN nanotubes are -2.06 and -2.08 e, respectively, for smaller inter-defect distances (< 20 Å) vs. -1.97 and -1.98 e for larger distances (> 20 Å). The latter may be considered as more reliable charges where inter-defect interaction is practically absent. Formation energies of a single $F$ centre onto relaxed AlN nanotubes are found to be 7.2 and 7.1 eV for armchair- and zigzag-type chiralities, respectively (Table 2).

| Properties | Bulk | Graphitic sheets | Nanotubes (Fig. 3) |
|------------|------|-----------------|-------------------|
| $r_{F-Al}$, Å | -0.10 | -0.11 | -0.17 |
| $r_{F-N}$, Å | -0.03 | -0.03 | -0.05 |
| $\Delta q_{F}$, e | -1.82 | -1.78 | -1.86 |
| $E_{form}(F)$, eV | 8.8 | 8.6 | 7.2 |
| $\Delta \epsilon_{max}$ (CB), eV | 3.1 (7.4) | 3.2 (7.2) | 2.8 (7.1) |

Table 2. Structural and electronic properties calculated for defective AlN bulk, surface and NTs [18]

| Properties | Bulk | Graphitic sheets | Nanotubes (Fig. 3) |
|------------|------|-----------------|-------------------|
| $r_{F-Al}$, Å | -0.10 | -0.11 | -0.17 |
| $r_{F-N}$, Å | -0.03 | -0.03 | -0.05 |
| $\Delta q_{F}$, e | -1.82 | -1.78 | -1.86 |
| $E_{form}(F)$, eV | 8.8 | 8.6 | 7.2 |
| $\Delta \epsilon_{max}$ (CB), eV | 3.1 (7.4) | 3.2 (7.2) | 2.8 (7.1) |

- a description is given at the beginning of Section 3
- b single-layer (0001) surface described by either armchair-type or zigzag-type supercells;
- c negative sign corresponds to inwards relaxation (towards F center);
- d these values are estimated for the largest inter-defect distances in NTs;
- e we consider here a band gap for defectless w-AlN(0001) slab [10].

Three sets of inter-defect distances repeated along the axes of both AlN nanotube chiralities were calculated by us [18]. However, we present the band structures for the two sets for each type of NT (Figs. 5a-d) since for the largest inter-defect distances (27.0 Å for armchair-type NT as well as 32.4 Å for zigzag-type chirality), the band structure almost coincides with that for the middle inter-defect distance (20.25 or 21.5 Å, respectively). The interaction between the defects in this case is found to be negligible since the energy dispersion of defect levels in both band structures (Figs. 5c,d) does not exceed 0.02 eV; thus, these defect levels look like straight lines. This allows us to conclude that for $d_{F-F} \geq 20$ Å, the periodic F centre can be described as a single defect. Moreover, for these distances, we observe similarity of band structures for both NT chiralities (Figs. 5c,d). The largest difference between the band structures of armchair- and zigzag-type NTs is observed for the smallest inter-defect distances (Figs. 5a,b). There are two defect levels induced by N vacancy inside the NT band gap: (i) $a_1$ level, consisting of mainly Al(3s) state partially hybridised with Al(3p), which lies ~3.1 and ~2.8 eV above the top VB for armchair- and zigzag-type structure, respectively; (ii) doubly-degenerate $t_2$ level, consisting of mainly Al(3p) with a partial contribution from Al(3s), which is located either 2.3-2.4 eV below the bottom of CB for armchair-type AlN NT, with a small state splitting (~0.1 eV), or 1.5 eV below the same bottom for zigzag-type AlN NT (with a large splitting, ~1 eV). In both band structures we observe a pair of levels split off the top VB (Figs. 5a,b), which consist of Al(3s) and partially Al(3p) states which are not present in band structures of perfect AlIN NTs (Fig. 4). When comparing our results with the band structure of 1 nm thick zigzag-type SW NT recently calculated by Simeoni, etc. [17] we conclude that due to underestimate of band gap in that study both $a_1$ and $t_2$ levels are too close to CB bottom although their position relative to the top VB is qualitatively close to our results (2.25 vs. 2.8 eV). For zigzag-type AlIN NT with small inter-defect distances (Fig. 5b) the largest inter-defect (or defect-VB&CB) gap is found to be ~2.2 eV (cf. 7.0 eV for the whole band gap), for large
inter-defect distances this gap increases up to 2.8 eV. This means that the higher is the F centre concentration (in at least zigzag-type AlN NT), the closer its electronic properties to graphitic sheet.

4. Conclusions
Our results show that the larger the diameter of AlN SW nanotube is, the closer its properties to AlN thin film which can be considered as NT of infinite diameter. The zigzag-type chirality is energetically more favourable over armchair-type nanostructure in both regular and defective AlN NTs being
probably prevalent in experimentally synthesized nanomaterials. We have established a separation
limit for an isolated defect in AlN NTs (20 Å); on the other hand, the larger the content of $F$
t centres in NT is, the smaller its inter-defect energy gap as compared to perfect nanotubes of the same diameter.

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