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Stability and electronic structure of InN nanotubes from first-principles study*

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The stability and electronic structure of hypothetical InN nanotubes were studied by first-principles density functional theory. It was found that the strain energies of InN nanotubes are smaller than those of carbon nanotubes of the same radius. Single-wall zigzag InN nanotubes were found to be semiconductors with a direct band gap while the armchair counterparts have an indirect band gap. The band gaps of nanotubes decrease with increasing diameter, similar to the case of carbon nanotubes.

Keywords: InN, strain energies, band gap, first-principles calculation
PACC: 6185, 7115H, 7115M, 7280E

1. Introduction

Since the discovery of carbon nanotubes,[1] numerous researches has been carried out to synthesize new materials in nanometre-scale tubular form and to study their properties experimentally or theoretically. Of particular importance is to relate their microscopic property with the macroscopic performance. Cohen and co-workers evaluated the strain energies of BC_3 nanotubes and found that all BC_3 nanotubes, whether in zigzag or armchair form, were direct-band-gap semiconductors.[2] The technical importance of silicon promotes studies of silicon nanotubes. Electronic properties of hypothetical silicon nanotubes were firstly studied in comparison with carbon nanotubes by Fagan and Barierle.[3] Singh and Briere[4] proposed a hexagonal silicon nanotube which can be stabilized by doping with 3d transition metals. Searching for nanotubes in group III nitrides is of technological interest and very promising. Shortly after the discovery of carbon nanotubes, based on the similarities between graphite and boron nitride (BN), Cohen and co-workers predicted the existence of boron nitride nanotubes by tight binding calculation.[5] This was soon confirmed by the subsequent successful synthesis of the multi-wall and single-wall boron nitride nanotubes. Using plasma-arc method, Chopra and Luyken[6] produced pure boron nitride multiwalled nanotubes with inner diameters in the order of 1 to 3 nanometres and with length up to 200 nanometres. Louiseau *et al*[7] further synthesized pure boron nitride nanotubes with few layers including single- and double- wall nanotubes. Recent experiments on the synthesis of AlN and GaN nanotubes have produced some exciting results. Tondare *et al* fabricated a tubular AlN with a diameter of around 50 nm using a highly nonequilibrium dc-ad plasma method.[8] Wu *et al* synthesized single-crystal faceted hexagonal AlN nanotubes with the length of a few micrometres and diameters from 30 to 80 nm.[9] The first-principles total energy calculation on the single-wall AlN nanotubes also indicated that the strain energies required to roll up graphitic sheet AlN into nanotubes are lower than that of carbon nanotubes and the band gap of AlN nanotubes depends strongly on the diameter (ranging from 2.84 to 3.95 eV).[10] Density function calculation on GaN nanotubes also reached similar conclusions on the possibility of formation of single wall GaN nanotubes.[11] In contrast to armchair AlN nanotubes, the energy band gap of armchair GaN seems less dependent on the diameter.

For group III nitrides in zinc blend or wurtzite structures, InN has much smaller electron and hole effective masses[12] than those of AlN[13] and GaN,[14] which makes it superior over AlN and GaN in applications such as high-frequency field-effect transistors.

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This situation may still be conserved in the case of nanoscaled tubular structures. In this paper we perform density functional total energy calculations on the band structures of graphitic sheet InN and single-wall InN nanotubes in zigzag and armchair forms. We evaluate the stability of InN nanotubes by the strain energy cost in order to wrap up graphitic sheet InN into a single wall nanotube and compare it with the result of carbon nanotubes. Our calculations indicated that the strain energies are smaller compared to the case of carbon nanotubes and all InN nanotubes are semiconductors with narrow band gaps.

2. Methodology

Our calculations were based on the density functional theory[15,16] using the plane wave method VASP.[17] The ion–electron interaction was described by the PAW (projector augmented waves) potentials[18,19] with PW91 generalized gradient approximation (GGA)[20] used as exchange-correlation function. The indium $4d^{10}$ electrons were included as valence electrons in order to enhance the transferability of the potential. The energy cutoff for the plane-wave expansion of wavefunctions is 520 eV and the period boundary condition is applied. Brillouin-zone integrations are done on ten special k points selected along the tube axis according to the Monkhorst and Pack scheme[21] using the Hermitian–Gaussian smearing technique[22] with the smearing parameter of 0.2 eV. We found that such parameters could ensure a convergence better than 0.1meV/atom. InN nanotubes are placed 12Å apart from each other to avoid possible couplings between images. The conjugate-gradient algorithm[23] was applied to fully relax the ions into their instantaneous ground state (Here the maximum force on individual atom is less than 0.01eV/Å). Binding energies were calculated as the energy difference per atom between atoms in a structure and that of isolated atoms and the strain energies were the difference of binding energies of nanotubes and graphitic sheet. As comparison, we also calculated the strain energies of armchair nanotubes with PAW potential with the same exchange correlation function with the same accuracy.

3. Results and discussions

We first calculated the structural parameter and binding energies of InN in wurtzite, zinc-blende, rocksalt and graphitic sheet structures. By our calculation, InN favours the wurtzite structure with 3.60 and 5.77Å for lattice constants a and c, respectively. The binding energy of zinc blende InN is –5.381eV/atom, only 0.03eV higher than that of wurtzite structure, with a nearest-neighbour distance of 2.19Å, or equivalently a cubic lattice constant 5.05Å, in agreement with other first-principles calculation and experimental results.[24–26] The binding energy of rocksalt InN is –5.176eV/atom, 0.201eV higher than that of zincblende InN, with a lattice constant of 4.70Å for ground state and is consistent with experimental results.[27] As for the InN graphitic sheet, the binding energy is –4.953eV/atom with a nearest-neighbour distance of 2.07Å. The contraction of the In-N distance in graphitic sheet was similar to the case of AlN and GaN.[10,11] The binding energy difference between zinc blende and graphitic sheet InN was 0.428 eV/atom, lower than that of AlN[10] but slightly higher than that of GaN.[11] The rocksalt InN exists at a high pressure of 12GPa.[27] This means that the graphitic sheet InN can only exist at a higher pressure.

We then calculated the strain energy per atom required to roll up a graphitic sheet into a tube. Both the armchair and zigzag InN nanotubes were considered. Periodic boundary conditions were applied with a vacuum space of 12Å between nanotubes. The strain energies of armchair and zigzag InN nanotubes were shown in Figure 1 along with that of armchair carbon nanotubes for comparison. The strain energies decrease with increasing diameters of the nanotubes as expected. The difference in the strain energies between the armchair and zigzag nanotubes was very

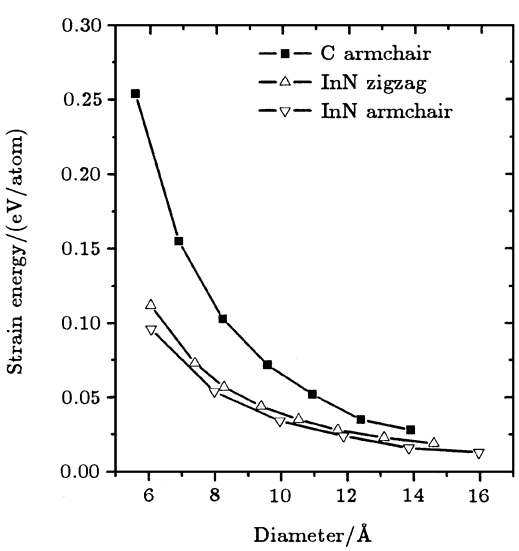


Fig.1. Strain energy vs diameter for the formation of InN zigzag and armchair nanotubes relative to their graphitic structure, with carbon armchair nanotubes for comparison.

small compared with that of carbon nanotubes.[28] The strain energies of carbon and InN nanotubes seem to be proportional to the inverse square of the diameter, which agree with previous reports on carbon nanotubes.[29] The fact that the strain energies of InN nanotubes are smaller than those of carbon nanotubes indicates the possibility of formation of InN nanotubes.

To study the electronic structures of InN nanotubes, we calculated the band structures of (5, 5) and (9, 0) InN nanotubes along the tube axis as shown in Fig.2. As expected, both are narrow-band-gap semiconductors. For the (5, 5) armchair InN nanotube, the conduction band minimum lies in Gamma point while the valence band maximum falls at the middle of the Brillouin zone, forming an indirect band structure

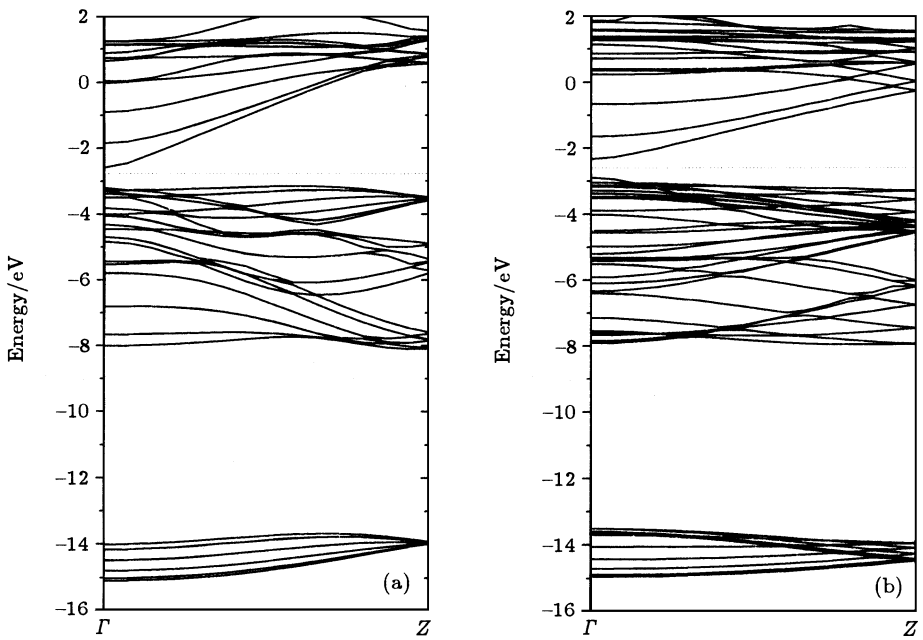


Fig.2. Band structures along the tube axis of (a) (5, 5) InN nanotubes and (b) (9, 0) nanotubes.

with a gap of 0.57eV. The (9, 0) zigzag InN nanotube possesses a direct band structure with a gap of 0.570eV. This means that such an InN nanotube may exhibit strong electroluminescence.

The diameter dependence of the band gap of zigzag and armchair InN nanotubes were also studied as shown in Fig.3. The calculations suggested that all zigzag InN nanotubes have a direct band structure while all armchair InN nanotubes have an indirect band structure. The gaps of both armchair and zigzag InN nanotube decrease with increasing diameters and saturate at 0.54eV which is the band gap of graphite sheet InN by our calculation, in contrast to the case of AlN and GaN where the band gap increases with increasing diameters.[10,11] The band gap of armchair InN nanotubes seemed to be less sensitive to the diameter change than that of zigzag InN nanotubes. This is consistent with the case of GaN nanotubes.[11]

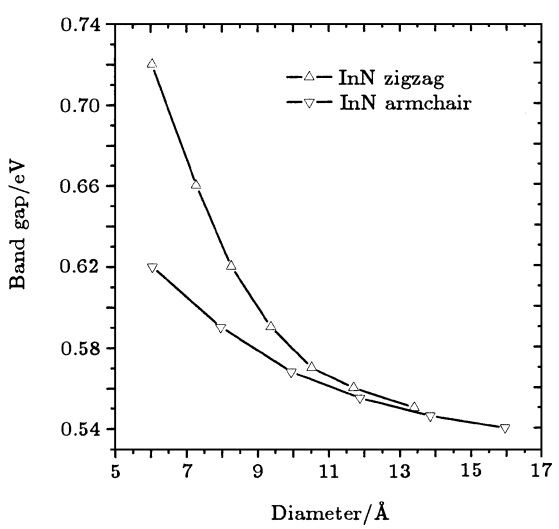


Fig.3. Diameter dependence of the band gap of InN zigzag and armchair nanotubes.

4. Conclusions

We have performed a first-principles study on the strain energies required to form InN nanotubes from InN graphitic sheet and their band structures. Our calculations indicate that InN graphitic sheet has an indirect band gap of 0.57eV and the strain energies are smaller than that of carbon nanotubes. The armchair InN nanotubes are narrow-gap semiconductors with indirect band structure while the zigzag nanotubes have a direct band gap. The band gaps of both armchair and zigzag InN nanotubes decrease with increasing diameters and saturate at the value of InN graphitic sheet. Our study on the property of InN nanotubes may be of help for exploitation of new materials in nanometre-scaled tubular form.

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