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Structural and electrical properties of selenium nanotubes

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ABSTRACT

The electronic structure calculations are systematically carried out within the density functional formalism for understanding the structural and electronic properties of a number of selenium nanotubes. In particular, single walled selenium nanotubes (achiral) are studied in this work. Our investigations reveal that the lower diameter nanotubes are unstable. Beyond certain diameter, the tubes retain their tubular structure and they show metallic property. Furthermore, work-functions of these tubes are found to depend on their diameters and differ from that of the bulk selenium surface.

1. Introduction

After the invention of carbon nanotube (CNT) in 1991 by Iijima [1,2], a new research area has emerged for the development of one dimensional nanostructures, i.e., nanowires and nanotubes. Due to their fascinating physical and electronic properties, the nanowires and nanotubes constitute an important class in nanoelectronics with their huge potential applications in nanoscale devices i.e., FET nonlinear devices, nanotube sensors etc. They may also be used as interconnects in circuit devices or for the purpose of thermo-ionic emission.

It has been realized that nanowires and nanotubes of materials other than carbon may also be used for various technological applications. Consequently, there has been tremendous interest in understanding the properties of nanowires, nanotubes of various materials using experimental as well as theoretical tools. For example, the nanotubes of Group-III nitrides, such as, BN, AlN, GaN [3–5] and several other nanotubes, such as, NiCl, TiO_2, SiC and Si [6–11] have been synthesized experimentally. On the other hand important theoretical investigations have been made on structural and electrical properties of C, Si, SiC, BeO, BN [12–16] nanotubes. Furthermore, theoretical investigations on the change of the functionality of nanotubes due to doping of various elements have been carried out. In this context, it may be mentioned that the change of functionality of CNTs due to the doping of metal and non-metal atoms [17–20] and that of Si nanotube due to the doping of transition metal has been studied extensively [21–23].

The synthesis of nanotubes made of non-carbon materials also includes selenium [24–28], gold [29] and platinum [30,31]. Gold and platinum are important noble metals while selenium is an important semiconducting material. It has wide applications in photocells, photographic exposure meters, medical diagnostics and xerography due to its high photoconductivity [32]. Its physical properties also include piezoelectricity, thermoelectricity, and nonlinear optical responses [33–35]. The synthesis of selenium nanotubes (SeNT) [24–28] thus motivates us to investigate its geometrical and electrical properties of various diameters. In the next section, we describe the system and the method that we adopt for calculations. Thereafter, we discuss the results of our calculation followed by a summary of our findings.

2. Method

The triangular lattice structure of selenium as shown in Fig. 1 is rolled to give a shape of a tubular structure. A SeNT is named as Se(n, n) if the $(0, 0)$ lattice point on the 2-D selenium sheet is joined to the (n, n) lattice point of the sheet in the process forming the tube. Thus, if the value of n is large, the corresponding tube diameter is large.

To understand the energetics of the minimum energy structures of Se(n, n), we carry out total energy calculations within the density functional theory at zero temperature. The VASP [36–40] code is used for this purpose. The wave functions are expressed by plane waves with the cutoff energy $|k+G|^2 \leq 350$ eV. The Brillouin Zone (BZ) integrations are performed by using the Monkhorst–

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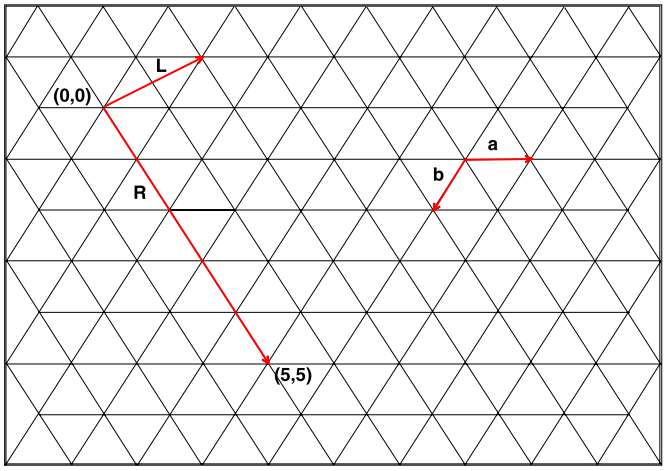

Fig. 1. The 2-D triangular network of Se(111) sheet having atomic thickness. The basis vectors of the 2-D network are $\vec{a}$ and $\vec{b}$ respectively. The circumference of Se(5, 5) is shown by R and the tube axis is along the vector $\vec{L}$.

Pack scheme with $40 \times 1 \times 1$ k-point meshes for a primitive cell. The convergence criterion for energy is considered to be less than 10^{-5} eV. All the calculations are performed in a periodically repeating supercell. The supercell size is taken to be $(n_{cell}L)$ Å $\times 30$ Å $\times 30$ Å to avoid interaction of a tube with its image where n_{cell} is the number of unit cell of the SeNT. In our study we have taken $n_{cell} = 2$. The convergence is achieved with the above parameters. Ions are represented by *PAW-vdWDF* pseudopotentials and results for fully relaxed atomic structures are obtained using the generalized gradient approximation (GGA). The preconditioned conjugate gradient method is used for the wave function optimization and the conjugate gradient method for ionic relaxation. All the atoms in the supercell are assumed to reach the relaxed positions when the force on each atom is less than 0.01 eV/Å.

3. Results and discussions

The selenium nanotubes, Se(n, n), with n ranging from 5 to 21 are considered for investigating their geometrical, mechanical and electrical properties. To obtain the energetically most favorable structure of a particular Se(n, n) tube, we construct ideal tubular structures with various Se–Se bond lengths and allow them to relax electronically as well as atomically completely. The binding energies per atom (BE) (which is defined below) of the relaxed structures of a particular Se(n, n) are noted as a function of the Se–Se bond length. The structure leading to the maximum BE correspond to the most favorable structure. For instance, the variation of the BE with Se–Se bond length for Se(6, 6) is recorded in Table 1 and plotted in Fig. 2. From Fig. 2, we note that the optimal bond length for Se(6, 6) is approximately 2.65 Å. However, note that the optimized bond length for Se(111) sheet is approximately 2.75 Å. Similar calculations are systematically done for finding out the most favorable structures of all the selenium nanotubes. The above mentioned BE is defined as

$$BE = -[E(\mathrm{Se}NT) - NE(\mathrm{Se})]/N$$

where $E(\mathrm{Se}NT)$ is the total energy of the selenium nanotube, $E(\mathrm{Se})$ is the total energy of the selenium atoms and N is the total number of selenium atoms. It is found that the BEs for Se(n, n) range between 2.04 to 3.32 eV (see Table 2) and they are plotted as a function of n in Fig. 4. The plot is oscillating for lower n tending to a saturation value for higher n. The diameters of the tubes, given in Table 2, are smoothly increasing with increase in n. We further observe that Se(5, 5) is unstable in the sense it does not

Table 1
The variation of binding energy per atom (BE) with bond length for Se(6, 6).

Bond length (Å)	BE (eV)
3.00	2.9326
2.95	2.9886
2.90	3.0039
2.85	3.0441
2.80	3.1345
2.75	3.2743
2.70	3.3801
2.69	3.4378
2.68	3.4493
2.67	3.4576
2.66	3.4598
2.65	3.4605
2.64	3.4576
2.63	3.4455
2.62	3.4412
2.61	3.4338
2.60	3.3995
2.55	3.2627
2.50	3.1838

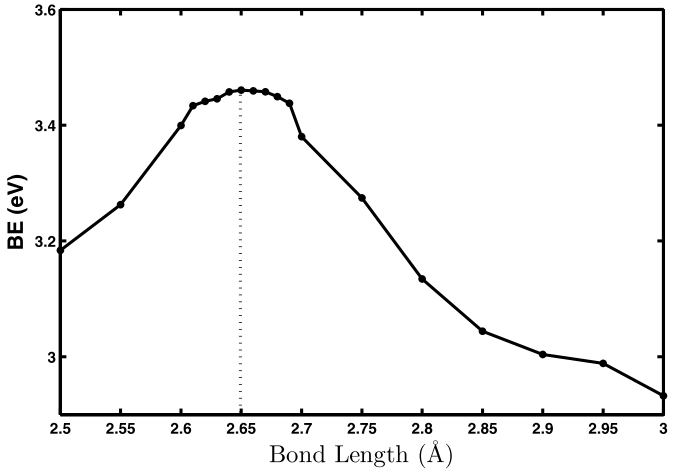

Fig. 2. The binding energy per atom of Se(6, 6) is plotted as a function of Se–Se bond length. The highest BE bond length turns out to be 2.65 Å.

remain in tubular form. However, the tubular structure is retained for Se(n, n) where $n > 5$. The relaxed structures of Se(6, 6) and Se(8, 8) are shown in Fig. 3. The average Se–Se bond lengths for the SeNTs are given in Table 2. The overall dispersion of the bond lengths about the average value is 0.15 Å. We have also calculated the curvature energies for all SeNTs to have the mechanical insight. The results are represented in Table 2. The curvature energy (E_c) is defined as the energy required to form a one-dimensional tubular structure by folding the 2D triangular Se(111) sheet and is calculated by using the following expression

$$E_c = [BE(sheet) - BE(\mathrm{Se}NT)].$$

The classical elasticity theory [41] says that E_c which is actually the mechanical tension of a nanotube should vary with diameter as $E_c = \alpha/(D^2)$. So we have plotted E_c as a function of $1/D^2$ in Fig. 5. However in this case there are fluctuations and the scattered data cannot be fitted in a straight line which implies that the system does not obey classical elasticity formula.

In addition to the structural properties of the selenium nanotubes, we have calculated the band structures of all the tubes. For example, we have shown the band structure plots of Se(6, 6) and Se(8, 8) in the left panels of Figs. 6(a) and (b) respectively. It is obvious from the figures that a few bands cross the Fermi energy level. The density of states plots of Se(6, 6) and Se(8, 8) (see right