LETTER TO THE EDITOR

Structures and electronic properties of ultrathin titanium nanowires

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Abstract
The structures of free-standing titanium nanowires are studied by using a genetic
algorithm with a tight-binding potential. Helical multi-walled cylindrical
structures are obtained and pentagonal packing is found for these thin wires
with diameters from 0.747 to 1.773 nm. The angular correlation functions
and vibrational properties of nanowires are discussed. We have further
calculated the electronic structures of the titanium nanowires with the plane-
wave pseudopotential method. Bulk-like continuous electronic bands are found
in the Ti wires thicker than 1 nm. The vibrational and electronic properties of
titanium nanowire are significantly dependent on the multi-walled structure of
the nanowire.

In the past decade, there has been considerable interest in metallic nanowires—both in the
fundamental low-dimensional physics and in technological applications such as molecular
electronic devices [1–16]. Most previous studies are focused on tip–surface contact [1–5]
or mechanically controllable break junctions [6, 7], which can be seen as very short metallic
nanowires. Recently, nanoscale metallic wires with well-defined structures and usable length
have been experimentally fabricated [8–12]. For instance, Takayanagi's group has successfully
produced suspended stable gold wires with various diameters and usable length. Novel helical
multi-shell structures are observed in these thinner gold nanowires [8–10]. Cu nanorods
with 1 μm length and diameters of several nanometres were deposited on substrates and
characterized [11]. By using carbon nanotube as a mask, Ti and Au nanowires a few
nanometres in width were produced by Ar^+-ion irradiation of Ti/Au thin layers [12]. Thus,
theoretical investigations on such free-standing metallic nanowires are important for future
studies. Tosatti's group has investigated the melting behaviour, non-crystalline structures, and
electronic properties of free-standing ultrathin Pb and Al nanowires [13–15]. We have recently
performed calculations on the structural, vibrational, electronic, and transport properties of Au
nanowire [16]. However, our present knowledge on the structure and electronic properties

of metallic nanowires is still quite limited. In particular, as far as we know, there is no theoretical work on the atomic structures and electronic states of unsupported long transition metal nanowires. In this letter, we shall investigate the structural, vibrational, and electronic properties of titanium nanowires with diameters (D) from 0.747 to 1.773 nm.

In our simulations, Ti nanowires of usable length are modelled by a supercell with a one-dimensional periodic boundary condition along the wire axis (z-) direction. As a reasonable compromise between discovering the helicity in the z-axis direction and avoiding the nanowire breaking into clusters upon relaxation, the length of the supercell is chosen to be 1.256 nm. We have tested different supercell lengths and found that the geometrical structures and helicity of nanowires do not sensitively depend on the chosen supercell length. The interaction between titanium atoms is described by a well-fitted tight-binding many-body potential [17]. To search for the most stable structures of nanowires globally, we adopt a genetic algorithm (GA) [16, 18, 19] based on molecular dynamics (MD). In the GA process, a number of initial configurations with arbitrary orientations are generated at random. Any two candidates in the population can be chosen as parents to generate a child wire by a mating operation [18]. The child configuration obtained is further locally relaxed by MD quenching and then selected to replace its parents in the population if it has lower binding energy. Usually 2000–10 000 GA iterations are sufficient to ensure a truly global minimum. The vibrational density of the nanowire is then calculated by diagonalizing the dynamical matrix for the optimized geometry.

On the basis of the lowest-energy structures, we perform density functional electronic structure self-consistent-field (SCF) calculations [20] with a plane-wave basis and an ultrasoft pseudopotential [21]. The electron density functional is treated in the local density approximation (LDA) and the energy cut-off of the plane-wave basis is chosen as 280 eV. The nanowires are placed in a supercell of 1.256 nm length in the z-direction, while the supercell lengths in the x-, and y-directions are chosen to be big enough to avoid the interaction between the nanowire and its periodic image. The Γ point is used to sample the Brillouin zone of the supercell. To check for possible magnetization in the wire, we have performed spin-polarized SCF electronic structure calculations without including the spin–orbit interaction. For the thinnest Ti wire, no spin polarization is found. All of the plane-wave pseudopotential calculations were performed by using the CASTEP program[1].

Figure 1 shows some typical Ti nanowire structures obtained from GA optimization. In general, the stable structures of titanium nanowires are multi-shell packings composed of coaxial cylindrical tubes (or shells). Each shell is formed by atom rows winding up helically side by side. The pitches of the helices for the outer and inner shells are different. The lateral surface of each shell exhibits a nearly triangular network. Such helical multi-shell structures have been theoretically predicted for Al and Pb nanowires [14] and recently observed in Au nanowires in experiments [10]. To characterize the multi-shell structures, one can introduce the notation n–n'–n''–n''' to describe the nanowire consisting of coaxial tubes with n, n', n'', n''' helical atom rows ($n > n' > n'' > n'''$) [10]. Thus the structures in figure 1 can be defined as 5–1, 6–1, 9–4, 12–6 –1, 17–12–6–1.

The structure of the thinnest 5–1 wire ($D = 0.747$ nm) in figure 1 is centred pentagonal, i.e., the outer shell contains five strands and the inner shell is a single row of atoms. It is worthy of note that small titanium clusters also show some experimental evidence for pentagonal or icosahedral structures [22]. The 6–1 ($D = 0.807$ nm), 12–6–1 ($D = 1.279$ nm), and 17–12–6–1 ($D = 1.713$ nm) wires in figure 1 constitute growth patterns with two-shell, three-shell, and four-shell hexagonal packings centred on a single-atom-row atom. In contrast, the

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[1] CASTEP is a density functional theory (DFT) package based on the plane-wave pseudopotential technique distributed by MSI.
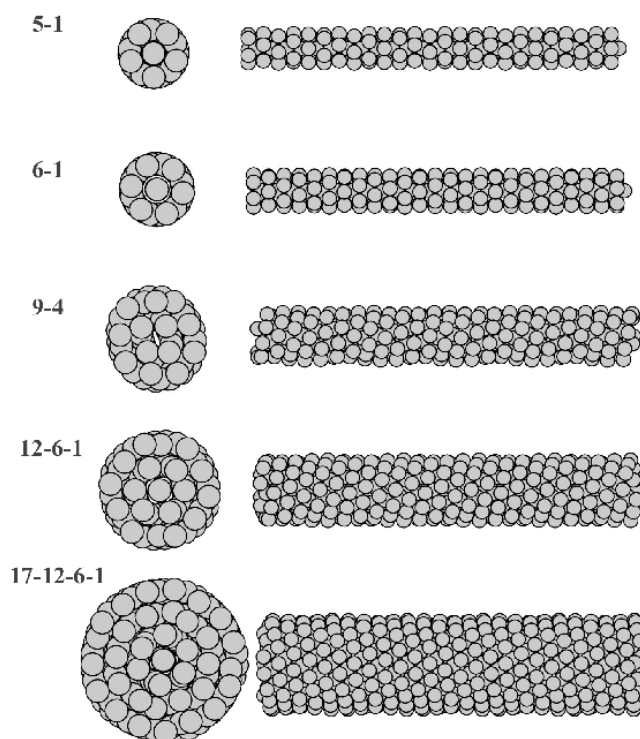
Figure 1. Morphologies of Ti nanowires with diameters from 0.747 to 1.713 nm. In each case, a top view (left) and side view (right) are presented. The helical multi-shell structures of the Ti wires can be identified as 5–1, 6–1, 9–4, 12–6–1, and 17–12–6–1 (see the text for details).

structure of the 9–4 wire ($D = 1.074$ nm) is composed by nine strands in the outer shell and four strands in the inner shell, without a single-atom row in the centre. It is natural to expect such structural difference to cause some modification of the physical properties, which will be discussed below.

The binding energy of the Ti atoms in the wires is about 90% of the bulk value. In our GA simulation, we have obtained numerous isomers and found that the helical ones are usually the lowest-energy configurations. The energy difference between non-helical structures and the helical lowest-energy state is about 0.006 eV/atom. For example, the binding energy for the helical 17–12–6–1 wire is −4.527 eV/atom while the lowest-energy non-helical configuration for such wire has a binding energy of −4.521 eV/atom (the bulk binding energy is −4.853 eV/atom [17]).

To further characterize nanowire structures, we present the angular correlation functions (ACFs) of these nanowires in figure 2. The features of deformed icosahedral structures can be found for the 5–1 wire, while perfect icosahedral-type packing should produce ACF peaks at 63.4°, 116.6°, and 180° [14]. The thicker wires starting from 6–1 demonstrate broad bond-angle distributions. There are two major peaks located around 60° and 120° that are related to the multi-shell hexagonal packing. In figure 2, there are considerable differences between the ACFs of the various wires, indicating that the titanium nanowires of various sizes may adopt different specific atomic structures.

Figure 3 shows the vibrational densities of states for the titanium nanowires. The vibrational bands of the thinner wires (5–1, 6–1) are rather discrete and molecule-like. As
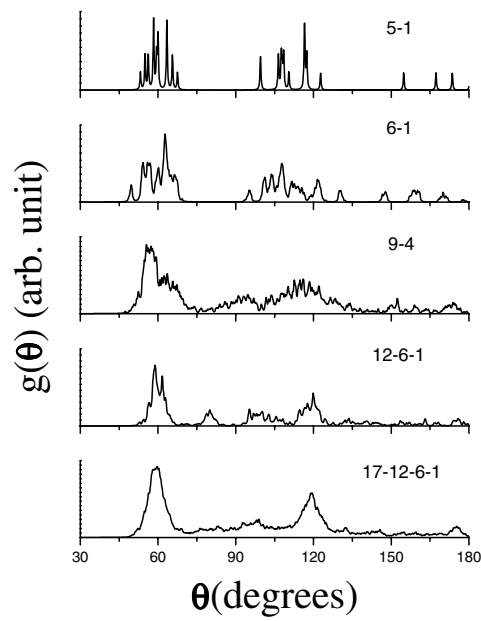
**Figure 2.** Angular correlation functions (ACFs) of titanium nanowires.
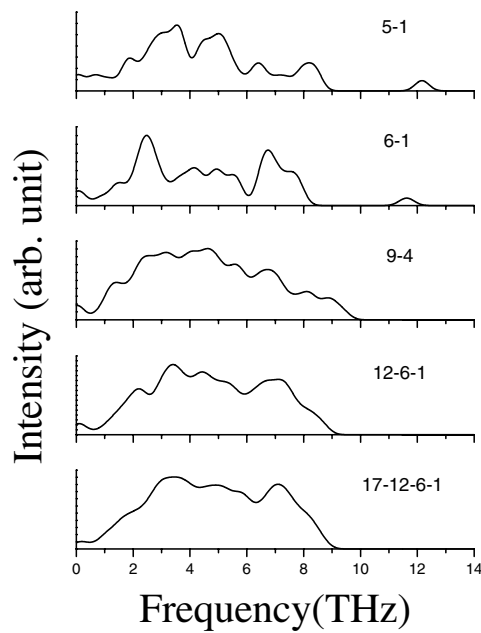
Figure 3. Vibrational densities of states of titanium nanowires.

the nanowire becomes thicker, the vibrational density of states gradually evolves with wire size (see the curves for the 12–6–1 and 17–12–6–1 wires in figure 3). The maximum peak at about 12 THz for the 5–1 and 6–1 wires disappears for the thicker wires and can be related to the inter-shell coupling, i.e., interaction between the outer five or six strands and the central

single-atom row. The vibrational spectrum of the 9–4 wire is remarkably differ from those for the other wires, although its diameter (1.074 nm) is quite close to that of the 12–6–1 wire (1.279 nm). This difference indicates that the vibrational coupling between the outer shell with nine strands and the inner shell with four strands in the 9–4 wire is quite different from the interaction between the outer shells and the central single-atom row. In another words, the vibration modes of titanium nanowires sensitively depend on the specific chirality of the constituent atomic strands.

In figure 4, we present the size evolution of the electronic density of states (DOS) for Ti nanowires. Like the vibration spectra, the electronic DOSs of the thinner nanowires (5–1, 6–1) are molecule-like and show some discrete peaks. In the 9–4 and 12–6–1 wires that are thicker than 1 nm, the discrete molecular levels start to overlap with each other and form bulk-like continuous electronic bands. This result is indirectly supported by a previous photoelectron spectroscopy study on size-selected Ti_n clusters [23]. It was found that the 3d band emerges at the Ti_8 cluster, beyond which the d band broadens and evolves towards the bulk band. The photoelectron spectrum of a 55-atom cluster ($D \sim 1$ nm) is already quite close to the bulk spectrum.
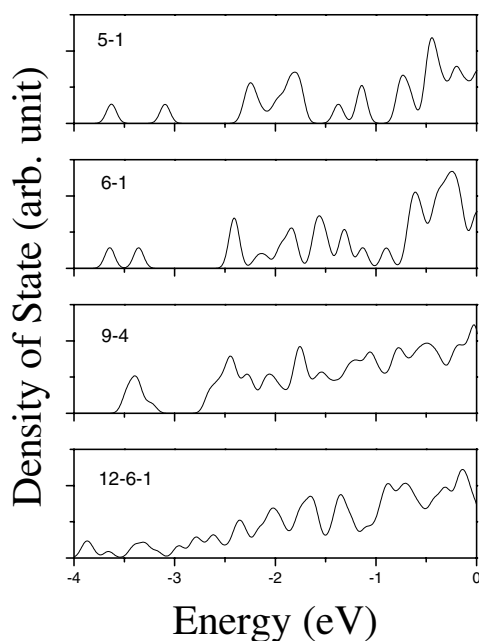
Figure 4. Electronic densities of states (DOSs) of titanium nanowires with 0.05 eV Gaussian broadening. The Fermi level is set as zero on the energy axis.

It is known that the 3d orbitals of titanium are relatively delocalized and participate in chemical bonding as valence orbitals [23]. Due to the participation of d electrons in chemical bonding and the directionality of d bonds, the nanowire cannot be simplified as a jellium cylinder with only s valence electrons. The influence of d electrons and the structural effect must be considered. In figure 4, we find a definite discrepancy between the electronic DOSs of 9–4 and 12–6–1 wires with only 0.2 nm difference in diameter. The structural sensitivities of the vibrational spectra and electronic states of titanium nanowires indicate some possible technological applications. One can modulate the physical properties of metallic nanowires by controlling the growth conditions and generating multi-shell nanowires with certain topologies.

Thus, the ultrathin nanowires with well-defined helical multi-shell structures are promising candidates for use in molecular electronics devices like carbon nanotubes. Calculations of the conductance of gold nanowire has revealed a relationship between wire conductance and wire geometry [16]. Our future work will investigate the conductance of the titanium nanowires, including different structures.

From the above results and discussion, we draw the following conclusions:

(1) helical multi-walled cylindrical structures are found for ultrathin titanium nanowires;
(2) pentagonal packings exist in the very thin wires while the thicker ones adopt hexagonal packing;
(3) vibrational properties of nanowires show gradual size evolution;
(4) the electronic states of smaller nanowires are molecule-like while the electronic structures of nanowires thicker than 1 nm demonstrate considerable bulk-like features;
(5) the physical properties of titanium nanowire depend on the structure and chirality of the constituent atomic shells.

We expect future experiments on titanium nanowires to validate our arguments.

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