NANO
LETTERS

2007
Vol. 7, No. 1
6−10

Nanocrystalline Nanowires: I. Structure

Philip B. Allen*

Department of Physics and Astronomy, Stony Brook University, Stony Brook, New York 11794-3800†, and Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973-5000

Received September 10, 2006; Revised Manuscript Received November 27, 2006

ABSTRACT

Geometric constructions of possible atomic arrangements are suggested for inorganic nanowires. These are fragments of bulk crystals, and can be called "nanocrystalline" nanowires (NCNW). To minimize surface polarity, nearly one-dimensional formula units, oriented along the growth axis, generate NCNWs by translation and rotation.

Periodic one-dimensional (1D) motifs are common in nature. The study of single-walled carbon nanotubes[1,2] is maturing rapidly, but that of other 1D systems is in an earlier stage. Inorganic nanowires are the topic of the present two papers. There is much optimism in this field.[3−6] Imaging gives insight into self-assembled nanostructures and incentives to improve growth protocols. Electron microscopy, diffraction, and optical spectroscopy on individual wires[7] provide detailed information. Device applications are expected. These systems offer great opportunities for atomistic modeling. Many specific calculations have been reported but have not greatly influenced the field. Theoretical difficulties include the fact that (1) the precise atomic structure of inorganic nanomaterials is rarely known, and (2) techniques to exploit rotational as well as translational symmetry are not much developed. The present paper (I) contains speculations about structure, which should assist in the construction of models. The subsequent paper (II)[8] shows by construction how rotational symmetry can be used to simplify both numerical tasks and conceptual understanding, with a particular example of vibrations worked out in detail.

If the surface and interior of a finite-diameter 1D nano-object is rigidly occupied by atoms, it is often called a nanowire or nanorod,[9] and is sometimes referred to as a "quantum wire" or "quantum rod.[10]" In this paper, the term nanowire is used; the root "wire" is not intended to imply metallic conductivity. Ordered nanowires fall into several structural classes: (1) helical nanowires, (2) molecular nanowires, and (3) nanocrystalline nanowires (NCNWs). Helical nanowires include carbon and related nanotubes, as well as other cases[11] where screw symmetries are more prominent than crystalline translations. Molecular nanowires may be fragments of quasi-1D crystals. For example, the materials[12] $M_2Mo_6X_6$, where M is an alkali and X is S or Se, may be made with nanoscopic transverse dimensions. The nonhelical inorganic polymer $(Mo_6S_6)_N$ is an example that has been studied experimentally[12] and theoretically.[13,14] Finally, NCNWs are 1D fragments of bulk crystals where the bulk is a three-dimensional (3D) (not a quasi-1D) material. These three categories are not exhaustive. There are also twinned,[15] "core−shell",[4,16] and longitudinally heterogeneous NCNWs. Filled nanotubes make up an intermediate category.[17]

The remainder of this note is about NCNWs. It offers a possible design principle, which assists in the visualization of candidate atomic structures, and provides a template for arrangements that can be tested theoretically, for example, by density functional theory. The basic idea is to (1) choose a maximally linear, charge-neutral, and (if possible) dipole-free atomic cluster containing a single formula unit, and (2) use, if possible, the symmetry axis of this linear cluster as the growth axis and distribute by translations and screw rotations the atomic clusters to give a stoichiometric nanowire with some symmetry around the growth axis and minimal surface polarity.

For monatomic crystals like Ag or Si, there are obvious candidate NCNW structures. For diatomics of AB stoichiometry, constraints arise from the possible polarity of the exposed surfaces.[18] Consider the wurtzite structure, which occurs in popular nanowires like CdSe, GaN, and ZnO. The lattice is hexagonal close-packed (hcp), with c/a not far from the ideal close-packed value of $\sqrt{(8/3)}$. If A atoms are on the hcp sites, then B atoms are placed "on top" (in the c direction) of A atoms, filling tetrahedral interstitial sites. A simple way to make a charge-neutral nanowire with nonpolar surfaces is by choosing the c-axis as the growth axis, and thinking of the wire as being built from c-axis-oriented AB pairs. In both hcp and wurtzite structures, wires may have an atom-centered C_3 axis, or a $(C_6|2/c)$ 6-fold screw axis passing through the vacant center of the puckered hexagon,[19]

---

* E-mail: philip.allen@stonybrook.edu.
† Permanent address.

10.1021/nl062139z CCC: $37.00

with $c/2$ being the screw displacement that accompanies each $2\pi/6$ rotation. Thus, c-axis-oriented wurtzite nanowires are an obvious choice for a NCNW structure, and are very favorable for theoretical modeling because of the symmetry.[20] Nature often cooperates, with c-axis growth being the most commonly reported morphology for wurtzite NCNWs. Akiyama et al.[21] compared, by computation, the energy of InP nanowires in the c-axis wurtzite geometry and the closely related (111)-axis zincblende geometry. Even though zincblende InP is more stable in bulk, the c-axis wurtzite nanowire is more stable for nanowires until the diameter exceeds a value near 12 nm. An explanation is that the (111)-axis zincblende structure, although equally charge-neutral, has extra corner dangling bonds not found in wurtzite. However, nature is extremely subtle. ZnO grows often in c-axis NCNWs, but can also adopt a very complex twinned wurtzite-type "nanobelt".[22] This form is then able to deform into "spring" geometry. The structure adopted by ZnO nanobelts is beyond what electronic structure theorists normally expect to predict.

Fluorite structure nanorods, such as CaF_2,[23] grow in (111) orientation. This is an example of the design principle. Once one of the four equivalent (111) axes is chosen, a linear F−Ca−F unit along this axis makes a good choice for the construction of a (111)-oriented nanowire by screw or simple 120° rotations around the growth axis, with nonpolar surfaces exposed.

TiO_2 forms NCNWs in both its rutile and anatase forms. These provide an excellent example of the organizing principles. Each Ti has six oxygens in octahedral arrangement. Both structures have a unique linear O−Ti−O unit; for each O atom bonded to three Ti atoms, one of the three Ti atoms has a special relation and a symmetry-equivalent O atom under inversion through the Ti. The special O atoms of a Ti atom are "axial", and the other four are "equatorial." In rutile, equatorial rectangles orient with one side vertical (c-axis) and share their horizontal sides with vertically translated TiO_4. There are two symmetry-equivalent TiO_6 octahedra per rutile cell, rotated by 90° around c, and translated by $(^1/_2, ^1/_2, ^1/_2)$. The axial O atoms have Ti−O bonds along (110) and $(1\bar{1}0)$ for the two octahedra, and serve as equatorial O atoms for two other Ti atoms. None of the three nearly orthogonal Ti−O bond directions of one octahedron is parallel to any Ti−O bond direction of the other octahedron.

The linear TiO_2 units are both charge-neutral and dipole-free. The difficulty with rutile is that there are two different orientations for the linear units. Therefore, unlike wurtzite or fluorite, the units cannot all align parallel to the growth axis to give nonpolar surfaces. The simplest and worst case is a (001) nanowire, shown in Figure 1. The simplicity is in the high symmetry. The undesirable part is the four equivalent polar (110) surfaces. The nanowire has no net dipole, but each surface has a dipole layer. As the nanowire grows outward, there are $(2n)^2$ TiO_2 units in each z-periodic double layer, or $(2n + 1)^2$ units if a Ti-atom-centered C_2 symmetry axis is used. It is also possible to make a C_4 screw-symmetric termination with $2n(n + 1)$ TiO_2 units per double layer, but these expose the less favorable (100) surfaces. The (001) axis does not seem to be a preferred growth axis of rutile NCNWs.

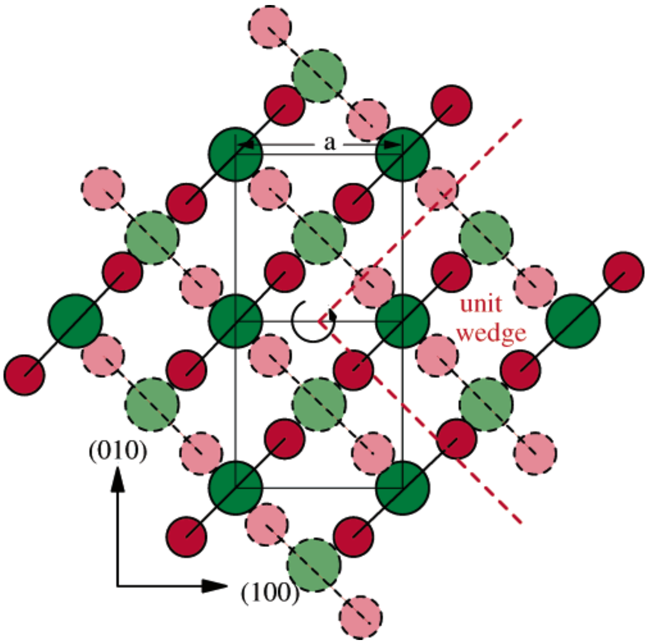

Figure 1. Atomic structure of a hypothetical rutile (001) NCNW, seen along the (001) growth axis. The structure has a C_4 screw axis with screw translation $c/2$, and four formula units of TiO_2 in the unit wedge. Ti atoms are in green, O atoms are in red; the lower layer has solid boundaries and bright colors. The upper layer is raised by $c/2$. This NCNW can be thought of as being built from linear TiO_2 units, shown connected by black lines, solid or dashed. Half of them have (110) orientation, and half have $(1\bar{1}0)$ orientation.

Another way to make a NCNW from rutile is shown in Figure 2. Here, the growth axis is (110), parallel to an axis of half of the TiO_2 units. This causes two of the four surfaces to be nonpolar (001), with four-coordinated Ti atoms and two-coordinated O atoms. The other two surfaces are polar $(1\bar{1}0)$, the same as in the (001) nanowire discussed above. Half of the $(1\bar{1}0)$ surface Ti atoms are four-coordinated, and half are six-coordinated. The latter have five fully coordinated oxygen neighbors and one dangling one-coordinated axial O atom. Real nanowires often have surfaces passivated by environmental adatoms, surfactant molecules, and so forth. It is desirable for theoretical models to mimic[24] this passivation, often by artificial constructs.[25] The model polar $(1\bar{1}0)$ surfaces of (110)-axis rutile can be passivated in a natural way[26] by adding H_2O molecules in equal numbers to the dangling O atoms. Then one H would associate to each O, and the other OH would occupy a vacant O position, since surface O sites are only half filled. Then the four-coordinated surface Ti atoms would become six-coordinated. The (110) axis is the reported growth direction for rutile NCNWs.[27]

The anatase form of TiO_2 is less stable than rutile but is easily produced in nanocrystalline form. Its crystal structure is especially favorable from the present point of view. Unlike rutile, in anatase, TiO_6 octahedra all have a linear O−Ti−O unit oriented along the c (or z) axis. In the square $a-b$ plane, there are alternate choices of O−Ti−O units, which are not quite linear, but are close enough, and always point in the x

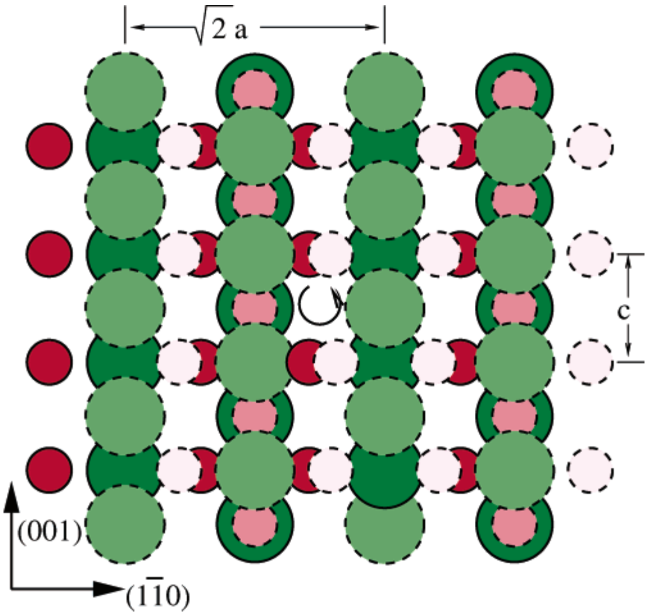

Figure 2. A hypothetical rutile (110) NCNW seen from the growth axis. The structure has both nonpolar surfaces ±(001), and polar surfaces $\pm(1\bar{1}0)$. The central axis is a C_2 screw axis, with screw displacement $a/\sqrt{2}$, which is half of the translational periodicity. If the (001)-direction had been shortened to eight instead of nine TiO_2 rows, the central axis would also have C_2 screw symmetry. Similarly, if the $(1\bar{1}0)$ direction had been changed from four to either three or five TiO_2 rows, the central axis would have simple C_2 symmetry.

and y directions. Therefore, any of these three choices of O−Ti−O units can be used to build a nanowire with nonpolar surfaces. The c-axis growth direction has the appealing property of a $(C_4|c/4)$ screw axis, or an alternative C_2 simple axis, whereas, for growth axes lying in the $a-b$ plane, the alternatives are $(C_2|a/2)$ or simple C_2 axes parallel to x or y. The (110) axis also has a C_2 simple rotational choice, but has no simple O−Ti−O unit to use for parallel construction of nonpolar NCNW surfaces. Anatase structure TiO_2 nanowires indeed grow in the (001)-axis orientation,[28] although (110)[29] and (101)-orientation[30] is also reported. The favorable surfaces of anatase (001) NCNWs might explain why nanophase TiO_2 is so often found in anatase instead of the bulk ground state structure, rutile.

The final example is perovskite (e.g., $BaTiO_3$). We have little direct experimental evidence of where atoms go in the nanowire. The (100) surface has two terminations: BaO and TiO_2. Both are nominally nonpolar. Experimental reports of (100)-oriented nanowires with probable (010) surfaces[31] and (110)-oriented nanowires[32] exist. A problem arises for candidate small (100) NCNWs. The standard symmetric cubic unit cell can be chosen with Ti (nominally 4+) at the center of a cube, eight nominally 2+ Ba ions on the corners, of which one-eighth of each is in the unit cell, and six nominally 2− oxygen ions on cube face centers, with half of each oxygen ion in the cell. By simple cubic translations, this unit is distributed to make an infinite crystal. But nature does not give fractional atoms or ions, so we cannot distribute this charge-neutral unit by translation to give a finite, locally charge-neutral nanosystem. Let us ignore charge-neutrality in favor of symmetry, letting adions or spare electrons provide the missing charge that unequally distributed ionic species require. Square $n \times n$ layers built from repeats of the square BaO and TiO_2 units yield (001) NCNWs with large deviations from stoichiometry when n is small. If we start from the Ba-cornered 2 × 2 unit and add layers by symmetric outward growth, we get the sequence of stoichiometries $Ba_9Ti_4O_{16}$, $Ba_9Ti_{16}O_{40}$, $Ba_{25}Ti_{16}O_{56}$, and so forth. If instead we start from a Ti-cornered 2 × 2 unit and grow symmetrically out, the sequence is $Ba_4Ti_9O_{21}$, $Ba_{16}Ti_9O_{33}$, $Ba_{16}Ti_{25}O_{65}$. In all cases, the oxygen concentration is one shy of the stoichiometric Ba plus twice Ti concentration, and the Ba-to-Ti ratio converges to 1 slowly, like $2/n$. Any small (100) perovskite NCNW has a large fraction of either highly undercoordinated Ba or Ti edge atoms. Modeling with adsorbed species like H^+ or OH^- may help.[33]

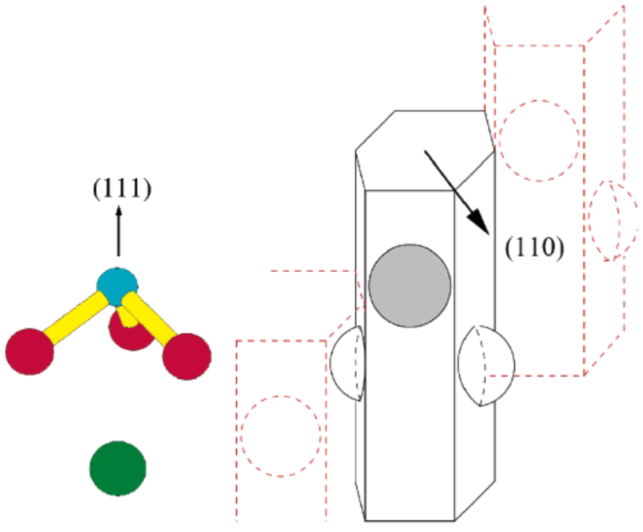

Figure 3. Cubic perovskite structure generated by translations of the formula unit shown on the left. This represents, for example, $BaTiO_3$, with the TiO_3 unit shown on top, with Ti on a C_3 rotational axis, and Ba below, on the same axis. The corresponding unit cell is shown to the right. It has three hemispherical protrusions (on alternate faces) to hold the formulaic oxygens, and three hemispherical holes, elevated by $c/3$ and rotated by 60°, to hold three virtual oxygens, which will appear under translations, to complete the TiO_6 octahedron. The translation rule is illustrated in Figure 4. Vertical translations by $c/3$ are enforced by the hemispheres. The dashed red lines indicate how stacking may terminate on a $(1\bar{1}0)$ oxygen-terminated surface, with oxygen sites being half occupied and half empty.

Consider cubic $BaTiO_3$ at temperatures above the ferroelectric distortive transitions. The aim is to pick a formula unit (one Ba, one Ti, and three O's) with maximal axial symmetry, and distribute them in an axially symmetric way. The answer is shown in Figure 3. It has the property of not only being charge neutral, but also having no net electrical dipole. This is important in $BaTiO_3$, which transforms at temperatures below 400 K in bulk crystals to a sequence of distorted phases whose separate domains each carry a spontaneous electrical polarization. The polarization can be organized, and eventually reversed, by an external field. Reversal is the hallmark of ferroelectricity. If the translational unit used to build the crystal or nanowire had a net dipole,

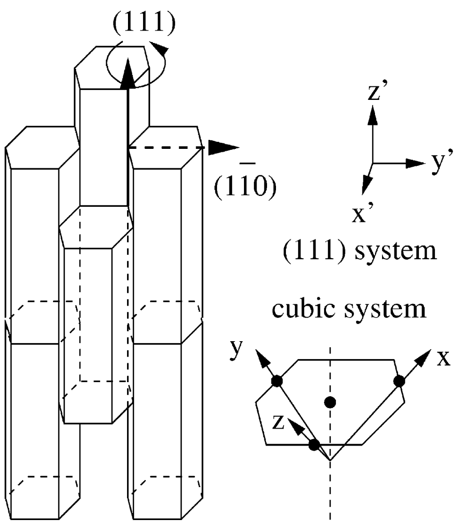

Figure 4. The simple cubic and related structures can be generated from the hexagonal prism unit cell shown, under cubic translations $n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$, where $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are $\mathbf{x}$, $\mathbf{y}$, $\mathbf{z}$ in the "cubic system," or $\mathbf{a}_n = a\sqrt{(2/3)}[\cos(2\pi n/3)\mathbf{x}' + \sin(2\pi n/3)\mathbf{y}'] + a\sqrt{(1/3)}\mathbf{z}'$ in the "(111)-system." The fcc and related structures can be similarly generated, except that $\mathbf{a}_1$ is $(a/2)(\mathbf{y} + \mathbf{z})$ and so forth. A nanowire with (111) growth direction is generated by terminating in transverse directions, with vertical facets formed by the sides of the hexagonal prisms, and a constant transverse cross-section. If the termination is symmetric around the (111) axis, there are two choices for the symmetry axis. The axis shown has $(C_3|c/3)$ screw symmetry, with screw translation $(c/3)\mathbf{z}$, where the c parameter is $\sqrt{3}a$ for perfect cubic angles. Alternately, a simple C_3 symmetry is found around an axis through the center of a hexagon.

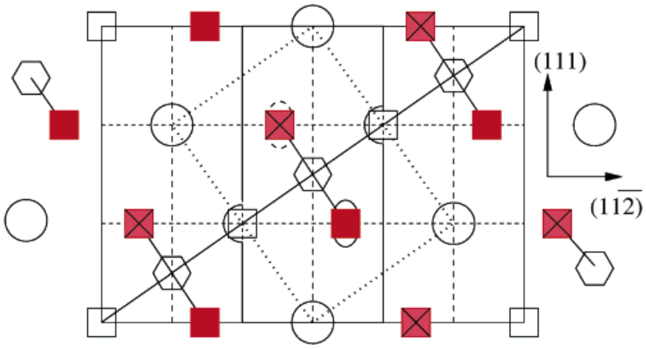

Figure 5. The perovskite $(1\bar{1}0)$ surface obtained by tiling the units of Figure 3 according to the rules of Figure 4. Ti atoms are denoted as hexagons, Ba atoms as circles, and oxygens as squares. Empty figures represent the subsurface BaTiO layer, and filled figures represent the top O_2 layer. This layer is half-filled according to the tiling rules of Figures 3 and 4. The missing atoms have "X" drawn through them. The diagonal rectangle shows the conventional primitive unit cell of the $(1\bar{1}0)$ surface. Vertical dashed lines are topmost edges of the hexagonal prisms. The central hexagonal prism, with protrusions and hollows indicated, is drawn in bold outline, and represents an alternate primitive surface cell. A few atoms to the left and right indicate how the surface would continue.

the structure would be pyroelectric rather than ferroelectric, and the polarity would not be reversible. The stability of the spontaneous polarity in nanowires of $BaTiO_3$ is a subject of debate.[33,34]

To construct a nanowire with this unit, one should use the (111) unit axis as the growth axis. This is not the reported growth direction, but perhaps perovskite nanowires with (111) growth can be made in the future. The unit cell for such a nanowire, with $(C_3|c/3)$ screw rotational symmetry, is shown in Figure 3. The exposed surfaces of such a nanowire are necessarily polar because the $BaTiO_3$ unit is not linear. The likely surface termination is (110), shown in Figure 5. Underneath this surface are alternating BaTiO and O_2 layers, with the top surface being a half-occupied O_2 layer. As in the rutile $(1\bar{1}0)$ surface, this can be passivated by the addition of a molecule like H_2O. One H goes on the existing O, and the remaining OH fills the site of the missing O atom. The surface is still polar, but has dangling bonds satisfied. It is not obvious whether nature will like this solution to the nanowire construction problem, but it offers a simple NCNW for theoretical modeling, and more satisfying solutions do not easily come to mind.

Acknowledgment. I thank J. W. Davenport, P. Gouma, J. Lauher, J. Mintmire, J. Misewich, J. T. Muckerman, M. R. Pederson, X. Shen, S. S. Wong, and J. Zheng for helpful discussions. Research at Brookhaven National Laboratory was supported by U.S. DOE under Contract No. DEAC 02-98 CH 10886. Work at Stony Brook was supported in part by NSF Grant No. NIRT-0304122, and by a BNL-SBU Seed Grant.

References

(1) Hamada, N.; Sawada, S.-I.; Oshiyama, A. *Phys. Rev. Lett.* **1992**, *68*, 1579.
(2) Saito, R.; Fujita, M.; Dresselhaus, G.; Dresselhaus, M. S. *Appl. Phys. Lett.* **1992**, *60*, 2204.
(3) Lu, J. G.; Chang, P.; Fan, Z. *Mater. Sci. Eng. Rep.* **2006**, *52*, 49.
(4) Yang, P. D. *MRS Bull. Feb.* **2005**, *30*, 85.
(5) Hu, J. T.; Odom, T. W.; Lieber, C. M. *Acc. Chem. Res.* **1999**, *32*, 435.
(6) Rao, C. N. R.; Deepak, F. L.; Gundiah, G.; Govindaraj, A. *Prog. Solid State Chem.* **2003**, *31*, 5.
(7) Wang, F.; Sfeir, M. Y.; Huang, L.; Huang, X. M. H.; Wu, Y.; Kim, J.; Hone, J.; O'Brien, S.; Brus, L. E.; Heinz, T. F. *Phys. Rev. Lett.* **2006**, *96*, 167401.
(8) Allen, P. B. *Nano Lett.* **2007**, *7*, 11.
(9) Neither "nanowire" nor "nanorod" appears in the 2006 AIP PACS (Physics and Astronomy Classification Scheme) index. It has become common in the literature to find the designation "nanowire (nanorod)." The implication is that nanowire is the preferred terminology, and nanorod means nothing different.
(10) The qualifier "quantum", applied to dots, wires, or rods, is ambiguous, not indicating whether the system is a free-standing fragment of a crystal or a region embedded in a host crystal, as in gate-patterned regions of a two-dimensional layer in a 3D crystal. It is preferable not to use "quantum" except for the latter case, or unless the ambiguity is intentional.
(11) Gulseren, O.; Ercolessi, F.; Tosatti, E. *Phys. Rev. Lett.* **1998**, *80*, 3775; Kondo, Y.; Takayanagi, K. *Science* **2000**, *289*, 606.
(12) Venkataraman, L.; Hong, Y. S.; Kim, P. *Phys. Rev. Lett.* **2006**, *96*, 076601. Tarascon, J.; Hull, G.; DiSalvo, F. *Mater. Res. Bull.* **1984**, *19*, 915.
(13) Ribeiro, F. J.; Roundy, D. J.; Cohen, M. L. *Phys. Rev. B* **2002**, *65*, 153401.
(14) Yang, T.; Okano, S.; Berber, S.; Tomanek, D. *Phys. Rev. Lett.* **2006**, *96*, 125502.
(15) Chen, H.; Gao, Y.; Zhang, H.; Liu, L.; Yu, H.; Tian, H.; Xie, S.; Li, J. *J. Phys. Chem. B* **2004**, *108*, 12038.
(16) Lauhon, L. J.; Gudikson, M. S.; Wang, D. Lieber, C. M. *Nature* **2002**, *420*, 57.
(17) Han, W.-Q.; Chang, C. W.; Zettl, A. *Nano Lett.* **2004**, *4*, 1355.
(18) Tasker, P. W. *J. Phys. C* **1979**, *12*, 4977.
(19) Tronc, P.; Stevanovic, V.; Milanovic, I.; Damnjanovic, M. *Phys. Status Solidi B* **2006**, *243*, 1750.
(20) Dalpian, G. M.; Tiago, M. L.; del Puerto, M. L.; Chelikowsky, J. R.; *Nano Lett.* **2006**, *6*, 501.

(21) Akiyama, T.; Nakamura, K.; Ito, T. *Phys. Rev. B* **2006**, *73*, 235308.
(22) Gao, P. X.; Ding, Y.; Mai, W.; Hughes, W. L.; Lao, C.; Wang, Z. L. *Science* **2005**, *309*, 1700.
(23) Mao, Y.; Zhang, F.; Wong, S. S. *Adv. Mater.* **2006**, *18*, 1895.
(24) Schrier, J.; Wang, L.-W. *J. Phys. Chem. B* **2006**, *110*, 11982.
(25) Huang, X.; Lindgren, E.; Chelikowsky, J. R. *Phys. Rev. B* **2005**, *71*, 165328.
(26) Onda, K.; Li, B.; Zhao, J.; Jordan, K. D.; Yang, J.; Petek, H. *Science* **2005**, *308*, 1154.
(27) Wu, J.-M.; Shih, H. C.; Wu, W.-T. *Nanotechnology* **2006**, *17*, 105.
(28) Lakshmi, B. B.; Patrissi, C. J.; Martin, C. R. *Chem. Mater.* **1997**, *9*, 2544.
(29) Zhang, X.; Yao, B.; Zhao, L; Liang, C.; Zhang, L.; Mao, Y. *J. Electrochem. Soc.* **2001**, *148*, G398.
(30) Mao, Y.; Wong, S. S. *J. Am. Chem. Soc.* **2006**, *128*, 8217.
(31) Yun, W. S.; Urban, J. J.; Gu, Q.; Park, H. *Nano Lett.* **2002**, *2*, 447.
(32) Mao, Y.; Banerjee, S.; Wong, S. S. *J. Am Chem. Soc*. **2003**, *125*, 15718. Wong, S. S. Stony Brook University. Private communication, 2006.
(33) Spanier, J. E.; Kolpak, A. M.; Urban, J. J.; Grinberg, I.; Lian, Q. Y.; Yun, W. S.; Rappe, A. M.; Park, H. *Nano Lett*. **2006**, *6*, 735.
(34) Geneste, G.; Bousquet, E.; Junquera, J.; Ghosez, P. *Appl. Phys. Lett.* **2006**, *88*, 112906.

NL062139Z