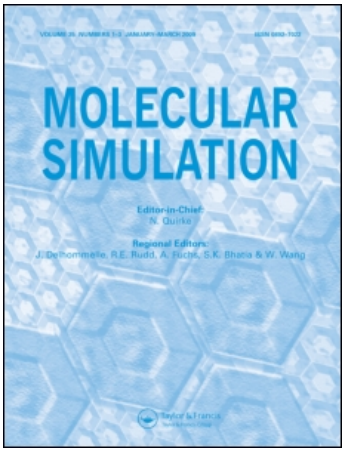


**Molecular Simulation**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

# An atomistic simulation study of cylindrical ultrathin Cu nanowires

Jeong Won Kang[a]; Ho Jung Hwang[a]
[a] Semiconductor Process and Device Laboratory, Department of Electronic Engineering, Chung-Ang University, Seoul, South Korea

Online publication date: 26 October 2010

**To cite this Article** Kang, Jeong Won and Hwang, Ho Jung(2002) 'An atomistic simulation study of cylindrical ultrathin Cu nanowires', Molecular Simulation, 28: 12, 1021 — 1030
**To link to this Article: DOI:** 10.1080/0892702021000011052
**URL:** http://dx.doi.org/10.1080/0892702021000011052

*Molecular Simulation*, 2002 VOL. 28 (12), pp. 1021–1030





# AN ATOMISTIC SIMULATION STUDY OF CYLINDRICAL ULTRATHIN CU NANOWIRES

JEONG WON KANG* and HO JUNG HWANG

*Semiconductor Process and Device Laboratory, Department of Electronic Engineering, Chung-Ang University, 221 HukSuk-Dong, DongJak-Ku, Seoul 156-756, South Korea*

*(Received October 2001; In final form November 2001)*

In order to understand the structure and properties of cylindrical ultrathin copper nanowires, we have simulated the growth of cylindrical copper nanowires using the steepest descent method, and investigated the energy per atom from changing the diameter, from spreading sheets, from the angular correlation function, and from the radial distribution function. The stable structure of the cylindrical ultrathin copper nanowires was found to be multi-shell packs composed of coaxial cylindrical shells with a {111} facet. As the diameter of the nanowire increases, the structural properties of nanowire becomes close to those of the bulk.

*Keywords*: Cu nanowires; Multi-shell nanowires; Atomistic simulations; Molecular dynamics

## INTRODUCTION

During the past decade, ultrathin metallic nanowires have been intensively studied because of the fundamental interest in their low-dimensional physics and technological applications, such as for molecular electronic devices [1–36]. Recently, long metallic nanowires with well-defined structures having diameters of several nanometers have been fabricated using different methods [8–13]. Novel helical multi-shell structures have been observed in ultrathin gold nanowires [8–11], and these have been investigated using molecular dynamics (MD) simulations [14–19]. Multi-shell nanowires have also been made from several inorganic layered materials, such as $WS_2$, $MoS_2$, and $NiCl_2$ [20–22]. The

*Corresponding author. E-mail: kok@semilab3.ee.cau.ac.kr.

ISSN 0892-7022 print 
DOI: 10.1080/0892702021000011052

cylindrical shells obtained in the MD simulations resemble the geometric shells of clusters. The MD simulations have focused on infinite wires with periodic boundary conditions along the wire axes. For example, MD studies have been carried out on the structure of ultrathin, infinite Pb and Al nanowires at $T = 0\,\mathrm{K}$ [23,24], on the pre-melting of infinite Pb nanowires orientated along the (110) direction [25], and on the melting of infinite Pt and Ag (100)-oriented nanowires [26]. The structure of freestanding Ti nanowires has been studied using a genetic algorithm and a tight-binding potential [27]. The strain rate effect induced by the amorphous disordering of pure Ni and NiCu alloy nanowires has also been investigated using MD simulation [28], as have the yielding and fracture mechanisms of Au and Cu nanowires [29,30].

Yanson *et al.* have studied multi-shell structures in Na nanowires [31]. The stability of the sodium nanowires was studied by modeling them as infinite uniform jellium cylinders, and by solving them self-consistently [32]. In addition, the deformation and breaking of an atomic-sized sodium wire using density functional simulation has been studied [33].

The stability of quasi-one-dimensional Si structures has been investigated using a generalized tight-binding MD scheme [34], and Si nanowires connected to Al electrodes have been studied using a large-scale local density functional simulation [35]. Bilalbegovic studied the room temperature structures of Al, Cu, and Au infinite nanowires using MD simulations, and showed that cylindrical multi-shell, and filled metallic nanowires exist for several fcc metals [19].

However, as far as we know, present knowledge on the structure and properties of metallic nanowires is still quite limited, and no theoretical work on the atomic structures of cylindrical ultrathin copper nanowires exists. Hence, computer simulations for ultrathin copper nanowires can help in the elucidation of their properties, and in the development of new methods for their fabrication. Computer simulations can also provide detailed microscopic information on the physical properties of ultrathin nanowires. In this work, we have investigated the structural properties of cylindrical ultrathin copper nanowires.

## SIMULATION METHODS

In our study on the structure of cylindrical Cu nanowires, we defined a cylinder with a known diameter, and then an atom was inserted into the bottom of the cylinder. Another atom was inserted into the bottom of the cylinder, and the atomic configuration was relaxed using the steepest descent (SD) scheme. After sufficient relaxation, another atom was inserted into the bottom of the cylinder, and atomic configuration was again relaxed using the SD scheme. This

simulation was repeated until the length of the nanowire reached 40 Å. The reflective boundary condition (RBC) and the free boundary condition were then applied to the radial direction of the cylinder and to the axis of the nanowire, respectively. The diameter of the cylinder, $D_c$, ranged from 2 to 16 Å, and the positions of the atomic centers were sited along the radius, $D_c/2$.

Copper atoms can be described by a well-fitted potential function of the second moment approximation of the tight-binding (SMA-TB) scheme [38]. This potential is in good agreement with other potentials, and with experiment, for bulk [38] and low-dimensional systems [37]. The physical values for Cu calculated by the SMA-TB agree with other theoretical methods, and those measured by experiment [37,43]. The SMA-TB-type potential function has previously been used in atomistic simulation studies of nanoclusters [38–42] and ultrathin nanowires [27].



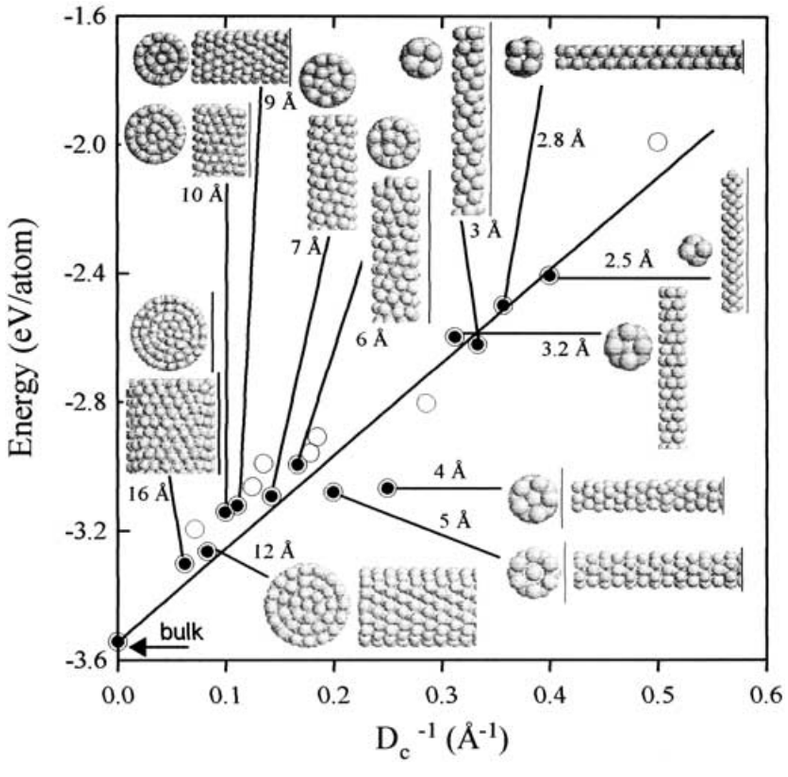


FIGURE 1 The total energy per atom, E, vs. the inverse cylindrical diameter, $l/D_c$, for the structures obtained by optimization of copper nanowires. Selected morphologies with a given $D_c$ are shown.

## SIMULATION RESULTS

Figure 1 shows the total energy per atom vs. the inverse cylinder diameter, $1/D_c$, for structures having the typical morphology of the cylindrical ultrathin nanowires obtained by our simulations. In general, the stable structures of the cylindrical copper nanowires are multi-shell packs composed of coaxial cylindrical shells. Some examples of the cylindrical copper nanowires include a single atom chain at their center. Each shell is formed by rows of atoms wound helically upwards, side by side. The pitch of the helices for the outer and the inner shells are different. The lateral surface of each shell exhibits a near-triangular network. Such helical multi-shell structures have been theoretically predicted for Al, Pb [23,24], Au [14–19], and Ti nanowires [27], and were recently experimentally observed in Au nanowires [8–11]. To characterize the multi-shell structures, we used the simple index of Kondo and Takayanagi (KT index) [10,27] using the notation $n$-$n'$-$n''$-$n'''$ to describe a nanowire consisting of coaxial tubes with $n$, $n'$, $n''$, $n'''$ helical atom rows [$n > n' > n'' > n'''$] The structures of the thinnest two nanowires ($D_c = 2.56$ Å), four nanowires ($D_c = 2.8 \sim 3.2$ Å), 5-1 nanowire ($D_c = 4$ Å), and 6-1 nanowire ($D_c = 5$ Å), are shown in Fig. 1. The 6-1, 8-3 ($D_c = 6$ Å), 9-4 ($D_c = 7$ Å), 11-6-1 ($D_c = 9$ Å), 13-8-3 ($D_c = 10$ Å), and 16-11-6-1 ($D_c = 12$ Å) wires constitute a growth pattern with a five-atom difference between the shells. In contrast, the structure of the 20-16-10-5-1 ($D_c = 16$ Å) wires constitute a growth pattern with a four-, five-, and six-atom difference between the shells, centered on a single atom chain. Shells having chirality without a single atom chain in the center compose the 8-3, 9-4, and 13-8-3 wires. Each nanowire has a {111}-like surface. Previous simulation work on nanowire elongation deformation showed that a rectangular {100} nanowire

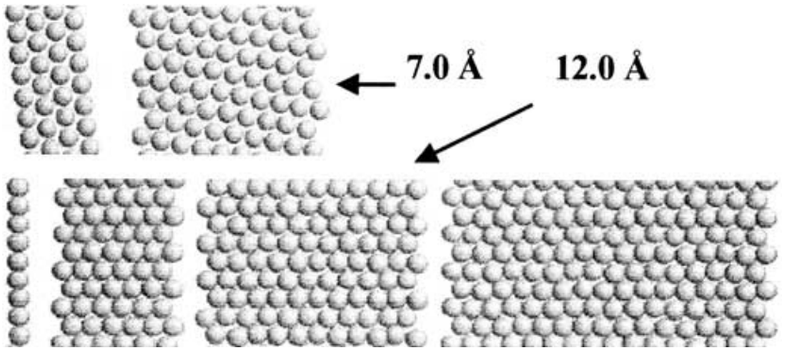


FIGURE 2 Spreading sheets of cylindrical Cu nanowires with $D_c = 7.0$ and 12.0 Å.

transforms into a cylindrical nanowire with {111}-like surface by stretching [30]. To carry out a more detailed study of cylindrical multi-shell nanowire structures, we investigated spreading sheets of nanowires. Figure 2 shows the spreading sheets of the 9-4 and 16-11-6-1 nanowires. Generally, the spreading sheets are composed of a triangular network. However, in the cases of $D_c = 8$, 14, 16 Å, triangular networks interlaced with rectangular networks, such as at grain boundaries, exist. In ultrathin gold nanowires, a square lattice and a triangular lattice were discovered by transmission electron microscope (TEM) studies [8]. Future experiments on copper nanowires are expected to provide the physical evidence of our simulations.

Although usage of the KT index is useful, and it is easy to determine multi-shell nanowire structures, the chirality of the nanowires cannot be characterized by the KT index. Therefore, to investigate the spreading of sheets, we used the index of Tosatti *et al.* (the *T* index) [16] for the triangular network sheet. The *T* index is denoted by an $(n, h)$ shell consisting of $n$ helical rows forming a maximal angle ranging from 30° ($n = 0$) to 0° ($h = n/2$) with the shell axis. The *T* index provides information on the chirality and the helical atom rows in the shells. The tube unit cell is given by the orthogonal vector $(n, h)$ and the wire axis vector $(p, q)$, in which $p : q = (n - 2h) : (2n - h)$, and $(h = n/2)$. All other tubes, except $(n, 0)$ and $(n, h/2)$, are chiral, and $(n, h)$ and $(n, n - h)$ are symmetrical with one another. At a constant $n$ value, the radius from the wire center to an atomic center is given by $d_0(n^2 + h^2 - nh)^{1/2}/2\pi$, and this decreases with increasing $h$ as the strands progressively align with the axis. Here, $d_0$ is the distance from the atomic center to the wire center. The total number of atoms per shell is $N =$

TABLE I The structural indexes of cylindrical ultrathin copper nanowires obtained by our simulations. $D_c$ is the diameter of cylinder, the KT index is the index of Kondo and Takayanagi [10], and the *T* index is the index of Tosatti *et al.* [16]

| | Structure indexes | |
|---|---|---|
| $D_c$ (Å) | KT index $n$-$n'$-$n''$-$n'''$-$n''''$ | *T* index orthogonal vectors |
| 2.5 | 2 | (2,0) |
| 2.8 | 4 | (4,2) |
| 3.0 | 4 | (4,1) |
| 3.2 | 4 | (4,0) |
| 4.0 | 5-1 | (5,0)(1,1) |
| 5.0 | 6-1 | (6,0)(1,1) |
| 6.0 | 8-3 | (8,1)(3,1) |
| 7.0 | 9-4 | (9,1)(4,2) |
| 9.0 | 11-6-1 | (11,0)(6,0)(1,1) |
| 10.0 | 13-8-3 | (13,1)(8,1)(3,1) |
| 12.0 | 16-11-6-1 | (16,0)(11,0)(6,0)(1,1) |
| 16.0 | 20-16-10-5-1 | (20,0)(16,0)(10,0)(5,0)(1,1) |

$2(n^2 + h^2 - nh)$, and the number in the central strand is $q$. The chirality angle is given by $\tan^{-1}(\sqrt{3}h/(2n - 1))$. In this paper, the central strand is denoted by (1, 1). Table I shows both the KT and the $T$ indexes for some of the cylindrical multi-shell nanowires obtained by our simulations. Using the KT index, nanowires with $D_c = 2.8$, 3.0, and 3.2 Å, are denoted by 4. However, using the $T$ index, nanowires with $D_c = 2.8$, 3.0, and 3.2 Å, are denoted by (4, 2), (4, 1), and (4, 0), respectively. This is because, as mentioned above, at a constant $n$ value, the wire diameter is linearly proportional to $(n^2 + h^2 - nh)^{1/2}/\pi$.

For improved characterization, we analyzed the angular correlation function (ACF) and the radial distribution function (RDF) relating to the structural properties of cylindrical ultrathin copper nanowires. Figure 3 shows the ACFs of cylindrical ultrathin copper nanowires. The dashed line, the case where $D_c =$ 16 Å, indicates the ACF of the bulk at 300 K. As the nanowire diameter increases, the ACFs of the nanowires become similar to the ACF of the bulk. In cases where the nanowires have KT indexes of 2 and 4, the peaks of the ACFs are different

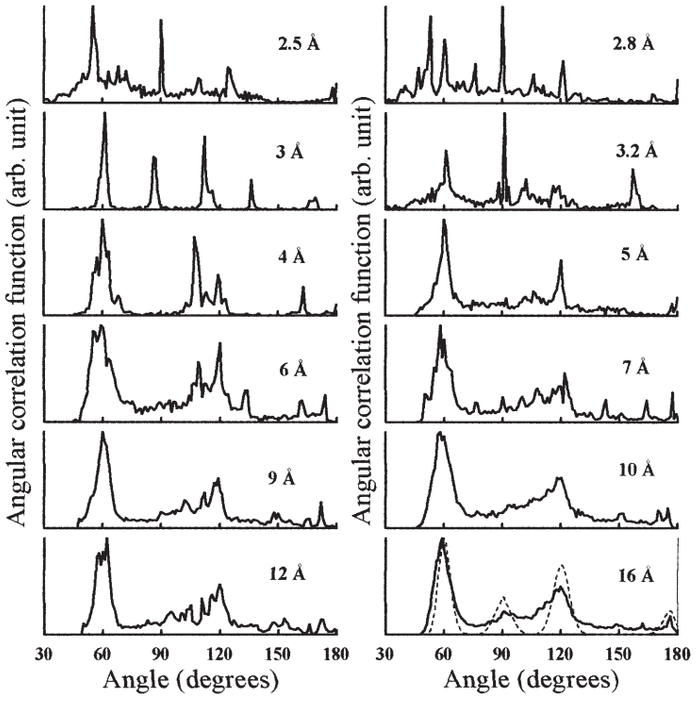


FIGURE 3 The Angular Correlation Function of the cylindrical ultrathin Cu nanowires shown in Fig. 1.

from the others at angles of about 90°, because they have a rectangular structure. Since the cross-sectional area of the 5-1 nanowire is related to a pentagonal structure, main peaks at about 60° (triangle) and 108° (pentagon), and small peaks at about 72° (pentagon) are observable. Since the outer shells have a triangular network, the ACFs of most of the multi-shell structure nanowires have their main peaks at about 60°. Since the cylindrical multi-shell nanowires do not have the fcc structure of the elementary metals, but have a new structure only observed in nanostructures, the ACFs of the nanowires are very different from the ACF of the bulk. In the cases where $D_c = 4$ Å, the ACFs of the nanowires do not show peaks at 90°, but show broad-angle distributions ranging from 90 to 120°.

Figure 4 shows the RDFs of Cu nanowires for different $D_c$ values. The dashed line in the case of $D_c = 16$ Å indicates the RDF of the bulk at 300 K. It can be seen that the nearest-neighbor atom distances are closer than those of the bulk. As the nanowire diameter increases, the RDFs of the nanowires become similar to the RDF of the bulk. The outstanding difference between the RDFs of the

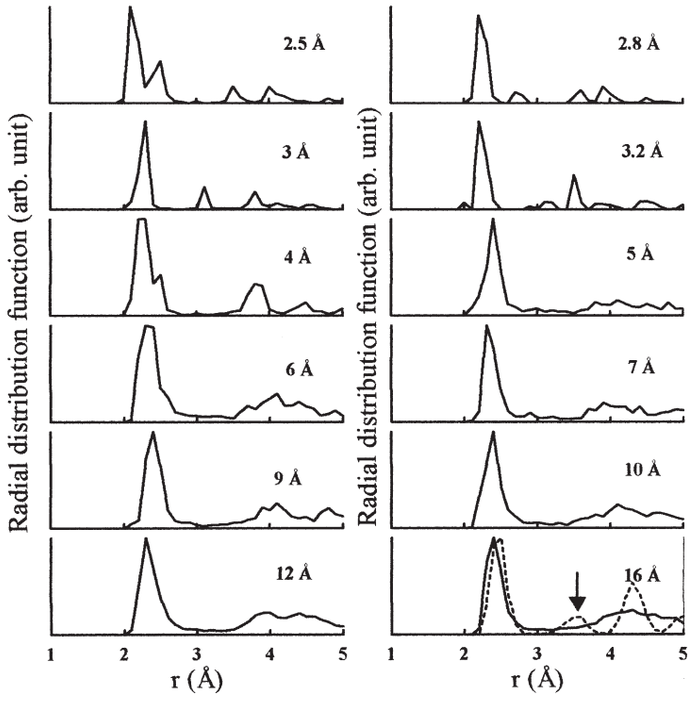


FIGURE 4 The Radial Distribution Functions of the cylindrical ultrathin Cu nanowires shown in Fig. 1.

nanowires and the RDF of the bulk is that the RDFs of the nanowires do not show any secondary peaks related to the second-nearest-neighbor correlation (lattice constant), as are seen in the bulk fcc materials. The arrows shown in Fig. 4 indicate these secondary peaks. The ACFs of the nanowires have a broader distribution than the ACF of the bulk, and the RDF peaks of the nanowires are hardly distinguishable from each other, except for the first RDF peaks.



## SUMMARY

We have simulated the growth of cylindrical ultrathin copper nanowires by using cylinders and the steepest descent method. The stable structure of the cylindrical ultrathin copper nanowires was composed of multi-shell packs of coaxial cylindrical shells. Investigation of spreading sheets of nanowires obtained by our simulations showed that a coaxial cylindrical shell can be obtained by circular rolling of a triangular network with an orthogonal vector. When the cylinder diameters were below 3.2 Å, the Angular Correlation Function showed a main peak at about 90°. The ACFs of the nanowires were very different from the ACF of the bulk. In cases where $D_c = 4$ Å, the ACFs of the nanowires did not show a peak at 90°, but rather, showed broad-angle distributions ranging from 90 to 120°. The RDFs of the nanowires did not show any secondary peaks, and the RDF peaks of the nanowires were hardly distinguishable from each other, except for the first peaks. However, as the diameter of the nanowire increases, the Angular Correlation and Radial Distribution Functions of the nanowires approached those of the bulk.

Our simulation of cylindrical ultrathin copper nanowire structures was limited by the conditions and methods used. However, our simulations showed the practical properties of nanowires. In the future, we expect more specific theoretical and experimental work will provide further information. This will elucidate thermal effects, electronic properties, and information from techniques such as TEM, which will overcome the limitations of our confined simulation work on copper nanowires.

### *References*

[1] Agrait, N., Rodrigo, J.G. and Vieira, S. (1993) "Conductance steps and quantization in atomic-size contacts", *Phys. Rev. B* **47**, 12345.
[2] Agrait, N., Rubio, G. and Bieira, S. (1995) "Plastic deformation of nanometer-scale gold connective necks", *Phys. Rev. Lett.* **74**, 3995.
[3] Rubio, G., Agrait, N. and Vieira, S. (1996) "Atomic-sized metallic contacts: mechanical properties and electronic transport", *Phys. Rev. Lett.* **76**, 2302.

[4] Yanson, A.I., Bollinger, G.R., Van den Grom, H.E., Agrait, N. and Van Ruitenbeek, J.M. (1998) "Formation and manipulation of a metallic wire of single gold atoms", *Nature* **396**, 783.
[5] Pascual, J.I., Mendez, J., Gomez-Herrero, J., Baro, A.M., Garcia, N. and Binh, V.T. (1993) "Quantum contact in gold nanostructures by scanning tunneling microscopy", *Phys. Rev. Lett.* **71**, 1852.
[6] Olesen, L., Laegsgaard, E., Stensgaard, I., Besenbacher, F., Schiotz, J., Stoltze, P., Hacobsen, K.W. and Norskov, J.K. (1994) "Quantized conductance in an atom-sized point contact", *Phys. Rev. Lett.* **72**, 2251.
[7] Kran, J.M., van Ruitenbeek, J.M., Fisun, V.V., Yan, J.K. and de Jongh, L.J. (1995) "The signature of conductance quantization in metallic point contacts", *Nature* **375**, 767.
[8] Kondo, Y. and Takayanagi, K. (1997) "Gold Nanobridge Stabilized by Surface Structure", *Phys. Rev. Lett.* **79**, 3455.
[9] Ohnishi, H., Kondo, Y. and Takayanagi, K. (1998) "Quantized conductance through individual rows suspended gold atoms", *Nature* **395**, 780.
[10] Kondo, Y. and Takayanagi, K. (2000) "Synthesis and characterization of helical multi-shell gold nanowires", *Science* **289**, 606.
[11] Rodrigues, V., Fuhrer, T. and Ugarte, D. (2000) "Signature of atomic structure in the quantum conductance of gold nanowires", *Phys. Rev. Lett.* **85**, 4124.
[12] Lisiecki, I., Filankembo, A., Sack-Kongehl, H., Weiss, K., Pileni, M.-P. and Urban, J. (2000) "Structural investigations of copper nanorods by high-resolution TEM", *Phys. Rev. B* **61**, 4968.
[13] Yun, W.S., Kirn, J., Park, K.H., Ha, J.S., Ko, Y.J., Park, K., Kim, S.K., Doh, Y.J., Lee, H.J., Salvetat, J.P. and Forró, László (2000) "Fabrication of metal nanowire using carbon nanotube as a mask", *J. Vac. Sci. Tehcnol. A* **18**, 1329.
[14] Wang, B., Yin, S., Wang, G., Buldum, A. and Zhao, J. (2001) "Novel structures and properties of gold nanowires", *Phys. Rev. Lett.* **86**, 2046.
[15] Bilalbegovic, G. (1998) "Structure and stability of finite gold nanowires", *Phys. Rev. B* **58**, 15412.
[16] Tosatti, E., Prestipino, S., Kostlmeier, S., Dal Corso, A. and Di Tolla, F.D. (2001) "String tension and stability of magin tip-suspended nanowires", *Science* **291**, 288.
[17] Bilalbegovic, G. (2000) "Structures and melting of infinite gold nanowires", *Solid State Commun.* **115**, 73.
[18] Torres, J.A., Tosatti, E., Dal Corso, A., Ercolessi, F., Kohanoff, J.J., Di Tolla, F.D. and Soler, J.M. (1999) "The puzzling stability of monatomic gold wires", *Surf. Sci.* **426**, L441.
[19] Bilalbegovic, G. (2000) "Metallic nanowires: multi-shell of filled?", *Comput. Mater. Sci.* **18**, 333.
[20] Tenne, R., Margulis, L., Genut, M. and Hodes, G. (1992) "Polyhedral and cylindrical structures of tungsten disulphide", *Nature* **360**, 444.
[21] Margulis, L., Salitra, G., Tenne, R. and Tallenker, M. (1993) "Nested fullerence-like structures", *Nature* **365**, 113.
[22] Hacohen, Y.R., Grunbaum, E., Tenne, R. and Tallenker, M. (1998) "Cage structures and nanotubes of $NiCl_2$", *Nature* **395**, 336.
[23] Gülseren, O., Ercolessi, F. and Tosatti, E. (1998) "Noncrystalline structures of ultrathin unsupported nanowires", *Phys. Rev. Lett.* **80**, 3775.
[24] Di Tolla, F., Dal Corse, A., Torres, J.A. and Tosatti, E. (2000) "Electronic properties of ultra-thin aluminum nanowires", *Surf. Sci.* **456**, 947.
[25] Gülseren, O., Ercolessi, F. and Tosatti, E. (1995) "Premelting of thin wires", *Phys. Rev. B* **51**, 7377.
[26] Finbow, G.M., Lynden-Bell, R.M. and McDonald, I.R. (1997) "Atomistic simulations of the stretching of nanoscale metal wires", *Mol. Phys.* **92**, 705.
[27] Wang, B., Yin, S., Wang, G. and Zhao, J. (2001) "Structures and electronic properties of ultrathin titanium nanowires", *J. Phys.: Condens. Matter* **13**, L403.
[28] Ikeda, H., Qi, Y., Cagin, T., Samwer, K., Johnson, W.L. and Goddard, W.A. (1999) "Strain rate induced amorphization in metallic nanowires", *Phys. Rev. Lett.* **82**, 2900.
[29] Mehrez, H. and Ciraci, S. (1997) "Yielding and fracture mechanisms of nanowires", *Phys. Rev. B.* **56**, 12632.
[30] Kang, J.W. and Hwang, H.J. (2001) "Molecular dynamics simulation study on mechanical properties of rectangular Cu nanowires", *J. Korean Phys. Soc.* **38**, 695.

[31] Yanson, A.I., Yanson, I.K. and van Ruitenbeek, J.M. (2000) "Supershell structure in alkali metal nanowires", *Phys. Rev. Lett.* **84**, 5832.
[32] Puska, M.J., Ogando, E. and Zabala, N. (2001) "Shell and supershell structures of nanowires: A quantum-mechanical analysis", *Phys. Rev. B* **64**, 033401.
[33] Nakamura, A., Brandbyge, M., Hansen, L.B. and Jacobsen, K.W. (1999) "Density functional simulation of a breaking nanowire", *Phys. Rev. Lett.* **82**, 1538.
[34] Menon, M. and Richter, E. (1999) "Are quasi—one dimensional structures of Si stable?", *Phys. Rev Lett.* **83**, 792.
[35] Landman, U., Barnett, R.N., Scherbakov, A.G. and Avouris, P. (2000) "Metal-semiconductor nanocontacts: silicon nanowires", *Phys. Rev. Lett.* **85**, 1958.
[36] Kang, J.W. and Hwang, H.J. (2001) "Mechanical deformation study of copper nanowire using atomistic simulation", *Nanotechnology* **12**, 295.
[37] Cleri, F. and Rosato, V. (1993) "Tight-binding potentials for transition metals and alloys", *Phys. Rev. B* **48**, 22.
[38] Michaclian, K., Rendon, N. and Garzon, I.L. (1999) "Structure and energetics of Ni, Ag, and Au nanoclusters", *Phys. Rev. B* **60**, 2000.
[39] Palacios, F.J., Iniguez, M.P., Lopez, M.J. and Alonso, J.A. (1999) "Molecular-dynamics study of the structural rearrangements of Cu and Au clusters softly deposited on a Cu(001) surface", *Phys. Rev. B* **60**, 2908.
[40] Rongwu, L., Ahengying, P. and Yukun, H. (1996) "Molecular-dynamics simulations of slow copper cluster deposition", *Phys. Rev. B* **53**, 4156.
[41] Li, T.X., Yin, S.Y., Ji, Y.L., Wang, B.L., Wang, G.H. and Zhao, J.J. (2000) "A genetic algorithm study on the most stable disordered and ordered configurations of Au38−55", *Phys. Lett. A* **267**, 403.
[42] Lei, H. (2001) "Melting of free copper clusters", *J. Phys.: Condens. Matter* **13**, 3023.
[43] Kang, J.W. and Hwang, H.J. (2001) "Molecular dynamics study of interaction between an energetic Al cluster and Al surface", *Phys. Rev. B* **64**, 014108.