A Possible Reaction Pathway to Fabricate a Half-Metallic Wire on a Silicon Surface

Yun Hao Lu, Hongmei Jin, Hongjun Zhu, Shuo-Wang Yang,* Chun Zhang, Jian Zhong Jiang, and Yuan Ping Feng*

Based on first-principles electronic structure calculations and molecular dynamics simulations, a possible reaction pathway for fabricating half-metallic Mo-borine sandwich molecular wires on a hydrogen-passivated Si(001) surface is presented. The molecular wire is chemically bonded to the silicon surface and is stable up to room temperature. Interestingly, the essential properties of the molecular wire are not significantly affected by the Si substrate. Furthermore, their electronic and magnetic properties are tunable by an external electric field, which allows the molecular wire to function as a molecular switch or a basic component for information storage devices, leading to applications in future molecular electronic and spintronic devices.

1. Introduction

As the downscaling of electronic devices continues, future computing and communication devices will be constructed using molecules or atomic clusters as building blocks.[1,2] A necessary step to realize this goal is fabrication of conductive and magnetic clusters or molecular wires on semiconducting or insulating substrates.[3] However, scientists have found themselves confronted with a dilemma. On one hand, function units such as molecules,[4–6] coordination compounds,[7] oligomers or polymers[8–11] with desired properties usually do not possess suitable functional groups which allow them to bind to the substrates. On the other hand, structures having such functional groups that facilitate strong surface adsorption typically exhibit poor electrical conductivity, because charge carriers tend to localize at these functional groups. Therefore, identifying the right molecular function unit and a matching substrate remains a challenge.

Through first-principles calculations, we demonstrate here a novel two-step assembly of molybdenum–borine (Mo–BBz) sandwich molecular wires (SMW) on Si(001) surface (**Figure 1**). Linear multiple decked sandwich molecular clusters (SMCs) which are formed by a metal atom sandwiched between two organic aromatic rings, and the corresponding one-dimensional (1D) sandwich molecular wires are attracting increasing attention.[12–22] These systems have been found to exhibit unusual electrical and magnetic properties, such as half-metallic, high-spin filter efficiency and negative differential resistance (NDR) effects.[15,17] They represent a new class of novel organic molecular magnets, which have been suggested as ideal candidates for the smallest possible high-spin magnets, with potential applications such as extremely high-density data storage.[23] Borine is chosen in the present study because of its very high reactivity and the fact that the B atom can easily facilitate binding on a substrate such as Si, compared to other aromatic rings where the strong C–H bond has to be broken in order for the aromatic rings to chemically bind to a substrate, in addition to the lattice matching issue.

As for the substrate, we chose silicon due to compatibility consideration with the current technology. Benefiting from the development of scanning tunneling microscope nanolithography technique, arbitrary arrays of silicon dangling bond on hydrogen-passivated silicon surface can be created via feedback

---

Dr. Y. H. Lu, Prof. J. Z. Jiang
International Center for New-Structured Materials (ICNSM)
Laboratory of New-Structured Materials
Department of Materials Science and Engineering
Zhejiang University
Hangzhou 310027, P. R. China
E-mail: luyh@zju.edu.cn

Dr. Y. H. Lu, Dr. C. Zhang, Prof. Y. P. Feng
Department of Physics
National University of Singapore
Singapore 117542, Singapore

Dr. H. Jin, Dr. S.-W. Yang
Institute of High Performance Computing
Agency for Science, Technology and Research
1 Fusionopolis Way, #16-16 Connexis, Singapore 138632, Singapore
E-mail: yangsw@ihpc.a-star.edu.sg

Prof. H. Zhu
Department of Applied Chemistry
College of Science
Nanjing University of Technology
Nanjing 210009, P. R. China

Dr. C. Zhang
Department of Chemistry
National University of Singapore
Singapore 117543, Singapore

Prof. J. Z. Jiang
State Key Laboratory of Silicon Materials
Zhejiang University
Hangzhou 310027, P. R. China

DOI: 10.1002/adfm.201202142

© 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

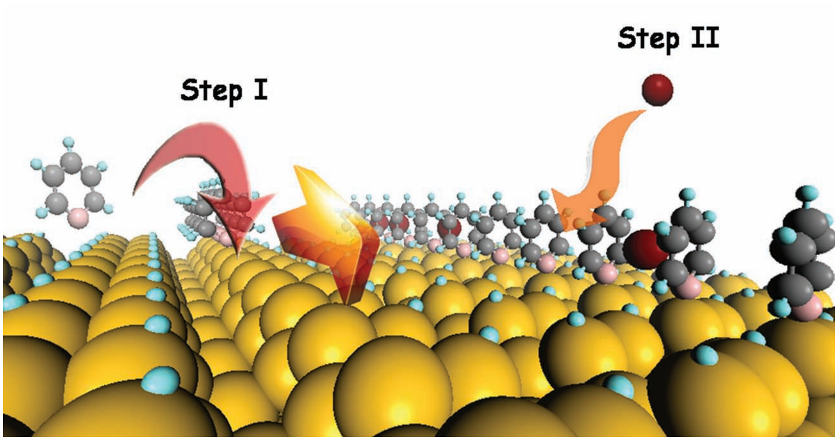

Figure 1. Schematic representation of the two-step assembly of sandwich molecular wires on a silicon surface. Borine first attaches to the Si substrate along the trenches in the [100] direction created by removal of hydrogen atoms, followed by insertion of Mo atoms between the borine atoms. Yellow, gray, pink, and cyan balls represent Si, C, B, and H respectively. Mo atoms are shown in dark red.

controlled lithography (FCL),[24–26] allowing accommodation of molecules along the dangling bond arrays on the Si surface. Formation of ammonia,[27] trimethylamine,[28] and pyridine[29] arrays on Si(001) and Ge(001) surfaces have been experimentally demonstrated. However, it is not easy for such nitrogen containing compounds to bond to the exposed surface silicon atoms continuously to form a long molecular array, because each surface Si atom has one un-paired electron but each nitrogen atom in aforementioned compounds posses a pair of electrons in its dangling orbital. Therefore, the additional electrons from the interface N–Si bonds migrate to the neighboring surface Si atoms, resulting in reconstruction of the silicon surface. As a result, the neighboring surface Si atoms rise up and become electron rich, which weakens the bonding between the nitrogen containing compounds and the surface Si atoms. In contrast, the B atom in the borine ring has an empty orbital which is extremely reactive, and can bond to an exposed surface silicon atom easily. Theoretical studies on formation of pyridine and borine 1D wires on hydrogen-passivated Si(001) surface [H–Si(001)][30] by Choi and Cho concluded that pyridine rings may bond to exposed surface silicon atoms alternatively, while borine rings are able to assemble on silicon surface and form continuous molecular array.[30,31] It is noted that the molecular arrays are formed here rather than molecular wires because the borine/pyridine rings are not chemically bonded to each other.

The Mo–BBz SMWs are assembled along the [100] direction on H–Si(001) in two steps, as illustrated in Figure 1. The borines are first attached to the Si substrate along the trenches in the [100] direction which is created by removal of hydrogen atoms, and subsequently the Mo atoms are inserted between borines. Our calculations predict that the (Mo–BBz)/H–Si(001) structure is stable up to room temperature. The system shows a half metallic behavior and its electrical conductance and spin polarization can be controlled via an external electric field (EEF) applied normal to the silicon surface. SMWs assembled on silicon surface avoids some major issues encountered by standalone molecular wires, such as instability due to surface absorption in conjugated organic molecules, carbon nanotubes or graphene,[32–34] and electrical migration in pure metal wires.[35,36] The (Mo–BBz)/H–Si(001) system would be an ideal candidate for molecular switch and information storage devices. These findings open a new avenue for fabricating molecular electronics or spintronics on traditional silicon based devices.

2. Results and Discussion

The H–Si(001) surface is a typical semiconductor substrate. As mentioned above, the surface H atoms can be removed by FCL. Following a FCL process in the [100] direction, the exposed surface Si atoms have alternate standing up and down dangling bonds. The highly active δ (p_z) orbital of the boron atom in borine allow it to form a chemical bond with a surface Si atom, similar to pyridines, which have been experimentally demonstrated to form arrays on a Si surface.[29] A molecular wire along the [100] direction of H–Si(001)[31] can thus be assembled, as illustrated in **Figure 2**a. Our calculations predict absorption energy of 1.79 eV per borine. The distance between two neighboring borines is constrained to the Si lattice (3.86 Å). At this separation, the interaction between the parallel borines is weak.

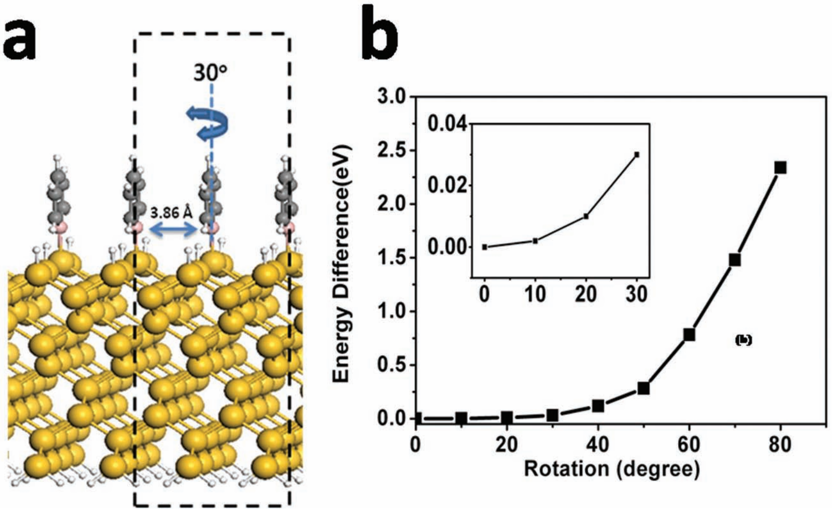

Figure 2. a) A side view of borine array absorbed on H–Si(001) surface along the [100] direction. b) Energy cost of rotating a borine around the B–Si bond, while the neighboring borines are fixed at their equilibrium positions. Yellow, gray, pink, and small white balls represent Si, C, B, and H, respectively.

© 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

it was predicted that borine tends to form dimers at 0 K.[30] In the present study, we also considered the rotation of borine around the B–Si bonds. Results of our calculations indicate that a borine can freely rotate within 20 degrees from its equilibrium position when its neighbors are fixed, beyond which the energy cost for rotation increases rapidly, as shown in Figure 2b.

It is known that the repeating unit of a SMW (or spacing between the organic rings) depends on the metal atom. To have a stable SMW assembled on the Si surface, it is important to find a SMW with a lattice that matches the Si(001) surface. We tested a series of SMWs formed with different first and second row transition metal atoms and found that the distance between two neighboring H–B (HBBz) in a standalone eclipsed 1D (Mo–HBBz)$_\infty$ is 3.61 Å, which is slightly smaller than the spacing between neighboring Si atoms in the [100] direction on the Si(001) substrate (Figure 2a). Considering that some room may be necessary to allow insertion of Mo atoms, we identify (Mo–BBz)/H–Si(001) as a promising structure. Our calculations indicate that the ground state of the standalone (Mo–HBBz)$_\infty$ is ferromagnetic (FM), and its energy is 128 meV lower than that of the antiferromagnetic (AFM) state. The calculated band structure (**Figure 3**a) shows that (Mo–HBBz)$_\infty$ is a half metal, with a band gap of more than 1.5 eV for the majority spin and a conductive minority spin channel, respectively. When (Mo–HBBz)$_\infty$ is stretched to match the lattice constant of the Si surface (3.86 Å), its band structure changes slightly but the half metallic feature remains (see Supporting Information Figure S1)

Experimentally, several techniques are available to produce singular Mo atoms. For example, it was reported that in a plasma enhancement chemical vapor deposition (PEVCD) atmosphere, a mixture of MoF_6 and hydrogen is capable of producing pure molybdenum deposits without fluorine surface contamination.[37] Additionally, DC magnetron sputtering technology can be used, with argon as the working gas, to produce Mo atoms or clusters, thereafter to deposit molybdenum films on soda-lime glass substrates.[38,39] Furthermore, laser vaporization is also capable of producing atomic Mo. Nagao et al. reported synthesis of the first bi-atomic sandwich molecular wire, i.e., $V_n(Cp)_{n+1}$ via laser vaporization technology.[40] It is reasonable to believe that the same method can be used to produce singular Mo atoms.

Insertion of the first Mo is simulated using a supercell with two units of Mo-BBz (**Figure 4** a). Due to the fact that borine can easily rotate or tilt, insertion of the first Mo is barrier-less and the process is exothermic. As a matter of fact, the total energy of the system is reduced by as much as 4.5 eV by the insertion of the first Mo atom (Figure 4a). The change in total energy includes the bonding energy of newly formed Mo-borine $\eta6$ bonds and an increase in the Si–B bonding energy. The Si–B bond is strengthened due to charge transfer from Mo to the borines. It is noted that the adsorption energy of Mo-BBz on silicon is 3.31 eV, which is significantly higher compared to that of adsorption of a singular borine (1.79 eV). The average energy released by Mo insertion is 2.78 eV. The process shown in Figure 4b corresponds to the insertion of the last Mo atom to complete the SMW. This would be the most difficult step because neighboring sites have been occupied by Mo and the borines become less flexible. Nevertheless, our calculations show that the barrier is small (0.24 eV) and can be easy overcome in such exothermic reaction. Since the remaining part of the silicon surface is fully passivated by H atoms, excess Mo atoms do not react with surface silicon atoms, and these Mo atoms/clusters as well as organic residuals on the surface can be washed away using routine wet cleaning processes in the manufacturing of semiconductors.[41,42]

Once the Mo–BBz is completely assembled on the H–Si(001) surface, Mo atoms form η^6 bonds with borines from both sides which restrict rotation and dimer formation by borines. The Mo atoms have been steadily locked at the centers of two neighboring borines. Meanwhile, all borines are bonded to surface Si atoms and are immobilized on the surface. Therefore, charge density waves (CDW) and Pierls effects are not expected to occur in this surface molecular wire which is different from the pure borine array on H–Si(001).[31] To verify the stability

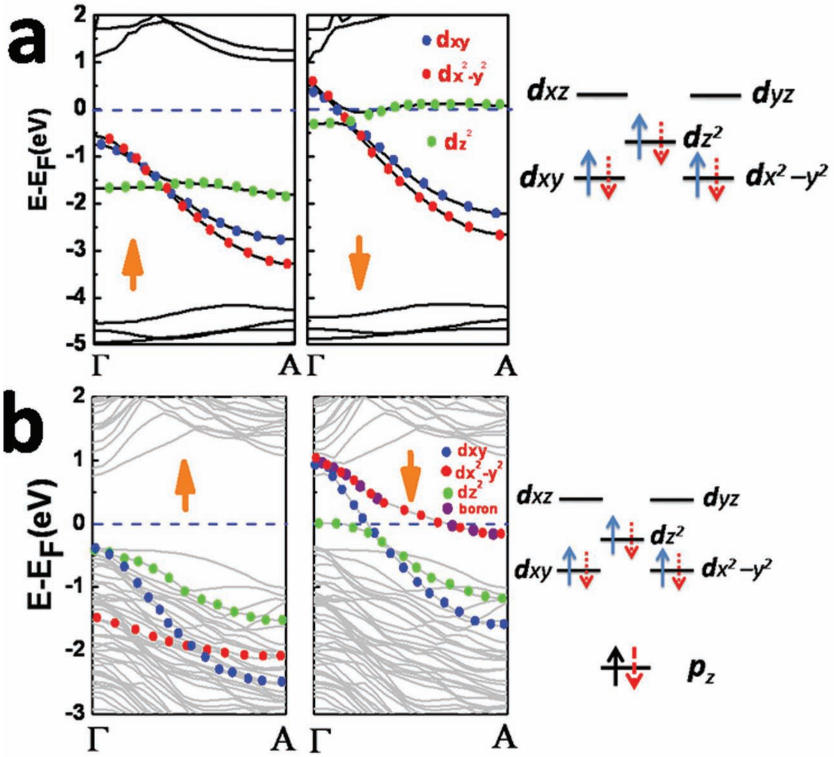

Figure 3. a) The band structure of (Mo–HBBz)$_\infty$ SMW, which shows half-metallic feature with a conductive spin-down channel (right panel) and a semiconducting spin-up (left panel) channel with a band gap >1.0 eV. The electron configuration of the Mo atom is schematically presented on the right, where the red dotted arrows denote partial occupation of the atomic orbital. b) The band structure of (Mo–BBz)/H–Si(001). The electron configurations on the Mo atom and the p_z orbital of the B atom are schematically presented on the right. The molecular wire remains half-metallic.

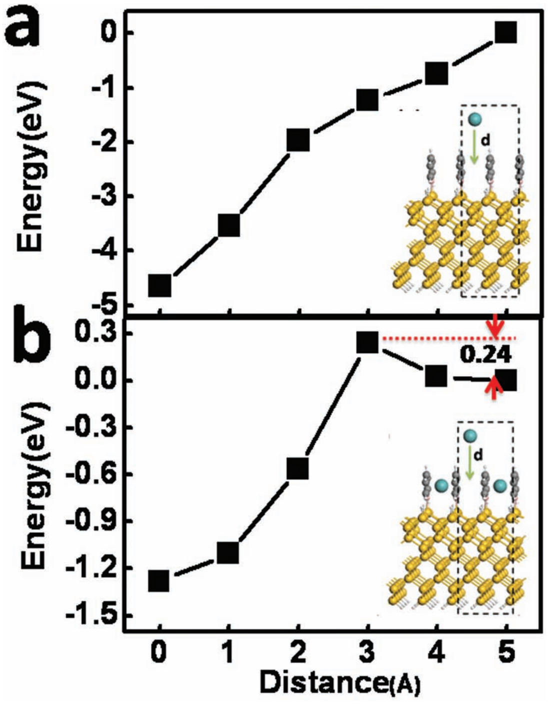

Figure 4. The energy profiles of inserting the a) first and b) final Mo atoms, respectively, into the borine array. The corresponding atomic models are shown as insets. Yellow, gray, pink, and small white balls represent Si, C, B, and H, respectively and Mo atoms are shown in cyan. Starting from an initial position which is 5 Å above the final equilibrium position, the Mo atom is moved along a straight path in steps of 1.0 Å. At each step, the vertical position of the Mo atom is fixed while all the other atoms are fully relaxed, except for those in the two bottom silicon layers, before the total energy is calculated.

of the SMW on H–Si(001) surface, we performed a molecular dynamics (MD) simulation at 300 K. A large model, including four borines and four Mo atoms was employed in the MD simulation (Supporting Information Figure S2a). The time-step used in the simulation was 0.3 fs. The variations of the total energy and the kinetic energy over a total simulation time of more than 3 ps (see Supporting Information Figure S2b) confirm that this surface SMW is stable on the H–Si(001) surface at least up to room temperature. Furthermore, Pierls distortion is not observed in the MD simulation.

Further calculations were carried out to investigate the electronic and magnetic properties of this surface SMW. Based on results of our calculation, (Mo–BBz)/H–Si(001) is half metallic with a band gap of more than 1.0 eV for the majority spin and a conductive minority spin channel, respectively (Figure 3b). In addition, the system exhibits stable FM coupling, even though the energy difference between the FM and AFM states (49.1 meV/unit) is smaller compared to that of the standalone SMW. The magnetic moment of 1.0 μ_B is mainly located in the Mo atom. It is noted that the conductive channel is mainly provided by 4d electrons of Mo atoms while the H–Si(001) surface retains its semiconductor characteristics.

Finally, we explore possible control of the electronic and magnetic properties of the (Mo–BBz)/H–Si(001) structure by a gate voltage. Electrical and magnetic switches controlled by an EEF are considered to be the key technologies in electronic and spintronic applications,[43] which will lead directly to low energy consumption devices.[44,45] To prevent dielectric breakdown in semiconductors, the applied electric field should not exceed 0.1 V/Å. However, considering that the field strength may be underestimated in the calculation, an electric field normal to the Si surface in the range of ±0.20 V/Å is considered in our simulation. It is found that before the EEF reaches 0.03 V/Å, the electronic and magnetic properties of the (Mo–BBz)/H–Si(001) system show little dependence on the field strength. The molecular wire remains essentially half-metallic and FM, with the magnetic moment only slightly decreased from 1.0 μ_B when the field is just below 0.03 V/Å. At the critical field strength of 0.03 V/Å, the surface SMW becomes a FM metal and its magnetization decreases to 0.55 μ_B/Mo. When the field strength is further increased from 0.03 V/Å, the system remains a FM metal with a magnetization close to 0.55 μ_B/Mo. At the same time, the Si surface remains semiconducting in the presence of the electric field and is not affected by the field.

Detailed analysis on the calculated band structures and density of states reveals that the transition from a half metal to a metal with an accompanied decrease in magnetization at the critical field strength of 0.03 V/Å is a result of charge redistribution within this wire-surface structure. Before the insertion of Mo atoms, the B–Si bond at the wire-surface interface is electron-poor since only one electron from the Si dangling bond is available for bonding. When a Mo is inserted between borines, Mo transfers one electron to borines and becomes Mo^+. Due to the formation of the Mo^+–$BBz^{\delta+}$ ionic structure, the electron from Mo is not entirely transferred to the p_z orbital of B atom to form a complete paired-electron B–Si σ bond, and the B–Si bond is still electron-deficient. The situation remains the same when a negative or a weak positive electric field is applied. In principle, Mo^+ ions should move up or down when a positive or negative EEF applied. In fact, due to η^6 bonding with borines on both sides, the Mo^+ ions are locked in their positions and hardly move relative to borines in response to the applied field. The effect of the field on Mo is mainly to shift the energy levels of its *d* bands. When the field strength approaches the critical value, i.e., 0.03 V/Å, some *d* electrons are drawn out from Mo and move down to the wire and surface interface, along with excess charges (δ+) in the borines, and start filling the B–Si bonds. Subsequently, a complete paired-electron B–Si σ bond is formed and the system becomes a FM metal.

3. Conclusions

We elucidated a feasible two-step reaction pathway to assemble a stable Mo-borine SMW on H–Si(001) substrate. The SMW is chemically bonded to the Si surface via the B–Si chemical bonds. Meanwhile, it retains its FM and HM properties which are not affected by the substrate. More interestingly, the system can be switched from half metallic to metallic by an EEF applied normal to the Si surface. This electric-field-tunable bistable states make the SMW potentially useful as an electrical switch and an information storage component. In the molecular wire–surface system, the metal atoms (Mo) provide the conductance channel and magnetization, while borine is used to chemically

© 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

bind the wire to the Si substrate. This novel concept of assembly of chemically bonded molecular wires on a semiconductor surface opens new window for fabricating molecular electronics/spintronics devices based on conventional silicon technology.

4. Models and Methodology

The model of borine absorbed on H–Si(111) along the [001] direction is shown in Figure 2a, where a periodic cell, including two absorbed borines and eight silicon layers is used for geometry optimization. The dangling bonds of Si at the bottom surface are saturated by hydrogen to simulate bulk silicon. The vacuum above the H–Si(001) surface is more than 20-Å thick, and the distance between molecular wires in neighboring supercells is >15 Å. A similar model was generated for (Mo–BBz)/H–Si(001) by inserting Mo atoms between borines (insets of Figure 4). Calculations on the standalone eclipsed 1D periodic $(\text{Mo–HBBz})_\infty$ was done by placing a unit of the molecular wire within a supercell of $20 \times 20 \times c'$ Å^3, where c' is the lattice constant of the molecular wire. Structural optimizations for all structures were performed using the Vienna ab initio simulation package (VASP)[46,47] without any constraint, and various methods, basis sets and parameters were carefully tested. The generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE)[48] scheme, including Coulomb interaction for Mo atom (U = 3.0 eV), was adopted for the exchange-correlation potential. The calculated electronic structures were further verified by the Hybrid functional based on a screened Coulomb potential (HSE06).[49,50] The projector augmented wave (PAW) is used to describe the interaction between ions and electrons.[51] The cutoff energy was set at 600 eV and a k-mesh of $1 \times 1 \times 60$ was used. The Hellmann–Feynman forces are converged to within 0.02 V/Å. The external electric field was simulated by a periodic saw-tooth-like electric-static potential.[52]

Test calculations were performed using eight and four layers of Si atoms for the substrate. The geometries and band structures of (Mo–BBz)/H–Si(001) obtained using the different substrate thicknesses show negligible difference. Therefore, a thin slab but a larger surface unit cell, including four borine rings and four Mo atoms, was used in molecular dynamics simulation to verify the structural stability of this (Mo–BBz)/H–Si(001) structure. Si atoms in the bottom two layers as well as the hydrogen atoms are fixed. Molecular dynamic simulation was performed in the NVT ensemble, using a Nose thermostat at 300 K. These settings are similar to those used in ref. [53].

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work is supported by a National Research Foundation (Singapore) Competitive Research Program (Grant No. NRF-G-CRP2007-05), National Natural Science Foundation of China (grant no. 11004171, 10979002, 50920105101, and 51050110136), National Key Basic Research Program of China (2012CB825700), and the fundamental research funds for the central Universities. Calculations were carried out at Shanghai Supercomputer Center (China) and Institute of High Performance Computing (Singapore).

Received: July 30, 2012
Revised: September 18, 2012
Published online: December 6, 2012

[1] C. Joachim, J. K. Gimzewski, A. Aviram, *Nature* **2000**, *408*, 541.
[2] J. R. Heath, M. A. Ratner, *Phys. Today* **2003**, *56*, 43.
[3] S. C. Erwin, F. J. Himpsel, *Nat. Commun.* **2010**, *1*, 58.
[4] V. J. Langlais, R. R. Schlittler, H. Tang, A. Gourdon, C. Joachim, J. K. Gimzewski, *Phys. Rev. Lett.* **1999**, *83*, 2809.
[5] R. Baer, D. Neuhauser, *J. Am. Chem. Soc.* **2002**, *124*, 4200.
[6] J. M. Tour, M. Kozaki, J. M. Seminario, *J. Am. Chem. Soc.* **1998**, *120*, 8486.
[7] Z. Ng, K. P. Loh, L. Li, P. Ho, P. Bai, J. H. K. Yip, *ACS Nano* **2009**, *3*, 2103.
[8] M. J. Crossley, P. L. Burn, *J. Chem. Soc., Chem. Commun.* **1987**, 39.
[9] M. J. Crossley, P. L. Burn, *J. Chem. Soc., Chem. Commun.* **1991**, 1569.
[10] L. Jones, J. S. Schumm, J. M. Tour, *J. Org. Chem.* **1997**, *62*, 1388.
[11] D. L. Pearson, J. M. Tour, *J. Org. Chem.* **1997**, *62*, 1376.
[12] F. Cervantes-Sodi, G. Csanyi, S. Piscanec, A. C. Ferrari, *Phys. Rev. B* **2008**, *77*, 165427.
[13] B. Huang, F. Liu, J. Wu, B.-L. Gu, W. Duan, *Phys. Rev. B* **2008**, *77*, 153411.
[14] T. Kurikawa, Y. Negishi, F. Hayakawa, S. Nagao, K. Miyajima, A. Nakajima, K. Kaya, *J. Am. Chem. Soc.* **1998**, *120*, 11766.
[15] S. S. Mallajosyula, P. Parida, S. K. Pati, *J. Mater. Chem.* **2009**, *19*, 1761.
[16] V. V. Maslyuk, A. Bagrets, V. Meded, A. Arnold, F. Evers, M. Brandbyge, T. Bredow, I. Mertig, *Phys. Rev. Lett.* **2006**, *97*, 097201.
[17] L. Shen, S. W. Yang, M. F. Ng, V. Ligatchev, L. P. Zhou, Y. P. Feng, *J. Am. Chem. Soc.* **2008**, *130*, 13956.
[18] L. Wang, Z. Cai, J. Wang, J. Lu, G. Luo, L. Lai, J. Zhou, R. Qin, Z. Gao, D. Yu, G. Li, W. N. Mei, S. Sanvito, *Nano Lett.* **2008**, *8*, 3640.
[19] Z. F. Wang, Q. Li, H. Zheng, H. Ren, H. Su, Q. W. Shi, J. Chen, *Phys. Rev. B* **2007**, *75*, 113406.
[20] X. Wu, W. An, X. C. Zeng, *J. Am. Chem. Soc.* **2006**, *128*, 12001.
[21] H. J. Xiang, J. L. Yang, J. G. Hou, Q. S. Zhu, *J. Am. Chem. Soc.* **2006**, *128*, 2310.
[22] L. Zhou, S.-W. Yang, M.-F. Ng, M. B. Sullivan, V. B. C. Tan, L. Shen, *J. Am. Chem. Soc.* **2008**, *130*, 4023.
[23] Y. Mokrousov, N. Atodiresei, G. Bihlmayer, S. Heinze, S. Bluegel, *Nanotechnology* **2007**, *18*, 495402.
[24] M. C. Hersam, N. P. Guisinger, J. W. Lyding, *J. Vac. Sci. Technol., A* **2000**, *18*, 1349.
[25] J. W. Lyding, T. C. Shen, J. S. Hubacek, J. R. Tucker, G. C. Abeln, *Appl. Phys. Lett.* **1994**, *64*, 2010.
[26] T. C. Shen, C. Wang, G. C. Abeln, J. R. Tucker, J. W. Lyding, P. Avouris, R. E. Walkup, *Science* **1995**, *268*, 1590.
[27] K. T. Queeney, Y. J. Chabal, K. Raghavachari, *Phys. Rev. Lett.* **2001**, *86*, 1046.
[28] M. Z. Hossain, S. Machida, Y. Yamashita, K. Mukai, J. Yoshinobu, *J. Am. Chem. Soc.* **2003**, *125*, 9252.
[29] Y. E. Cho, J. Y. Maeng, S. Kim, S. Y. Hong, *J. Am. Chem. Soc.* **2003**, *125*, 7514.
[30] J. H. Choi, J. H. Cho, *J. Am. Chem. Soc.* **2006**, *128*, 11340.
[31] J. H. Choi, J. H. Cho, *J. Am. Chem. Soc.* **2006**, *128*, 3890.
[32] A. K. Geim, *Science* **2009**, *324*, 1530.
[33] A. K. Geim, K. S. Novoselov, *Nat. Mater.* **2007**, *6*, 183.
[34] F. Schwierz, *Nat. Nanotechnol.* **2010**, *5*, 487.

© 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

[35] O. Akyildiz, T. O. Ogurtani, *J. Appl. Phys.* **2011**, *110*, 043521.
[36] T. O. Ogurtani, *J. Chem. Phys.* **2006**, *124*, 144706.
[37] G. Di Giuseppe, J. R. Selman, *J. Electroanal. Chem.* **2003**, *559*, 31.
[38] K. H. Yoon, S. K. Kim, R. B. V. Chalapathy, J. H. Yun, J. C. Lee, J. Song, B. T. Ahn, *J. Korean Phys. Soc.* **2004**, *45*, 1114.
[39] J. H. Scofield, A. Duda, D. Albin, B. L. Ballard, P. K. Predecki, *Thin Solid Films* **1995**, *260*, 26.
[40] S. Nagao, A. Kato, A. Nakajima, K. Kaya, *J. Am. Chem. Soc.* **2000**, *122*, 4221.
[41] D. Bohling, H. Treichel, T. Lazerand, A. Goldstein, M. George, *Technical Proceedings of the 2010 Clean Technology Conference, Clean Technology 2010* **2010**.
[42] C. Sheng-Hsiung, C. Shen-Li, C. Long-Yeu, Y. Wen-Kuan, 13th Int. Symposium on the Physical and Failure Analysis of Integrated Circuits, Singapore **2006** 129–132.
[43] Y. Yamada, K. Ueno, T. Fukumura, H. T. Yuan, H. Shimotani, Y. Iwasa, L. Gu, S. Tsukimoto, Y. Ikuhara, M. Kawasaki, *Science* **2011**, *332*, 1065.
[44] S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnar, M. L. Roukes, A. Y. Chtchelkanova, D. M. Treger, *Science* **2001**, *294*, 1488.
[45] I. Zutic, J. Fabian, S. Das Sarma, *Rev. Mod. Phys.* **2004**, *76*, 323.
[46] G. Kresse, J. Furthmuller, *Phys. Rev. B* **1996**, *54*, 11169.
[47] G. Kresse, J. Hafner, *Phys. Rev. B* **1993**, *47*, 558.
[48] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865.
[49] J. Heyd, G. E. Scuseria, M. Ernzerhof, *J. Chem. Phys.* **2003**, *118*, 8207.
[50] A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, G. E. Scuseria, *J. Chem. Phys.* **2006**, *125*, 224106.
[51] P. E. Blochl, *Phys. Rev. B* **1994**, *50*, 17953.
[52] Y.-H. Lu, L. Shi, C. Zhang, Y.-P. Feng, *Phys. Rev. B* **2009**, *80*, 233410.
[53] N. Jakse, A. Pasturel, *Phys. Rev. Lett.* **2003**, *91*, 195501.

© 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim