Charge Control of Surface Dangling Bonds Using Nanoscale Schottky Contacts

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ABSTRACT Titanium silicide ($TiSi_2$) nanoscale Schottky contacts were prepared on hydrogen-terminated n-type Si (100) surfaces. The Schottky contact created a region of upward band bending surrounding the $TiSi_2$ contacts. The surface band bending was observed as a sloping surface depression using the scanning tunneling microscope. Scanning tunneling spectroscopy measurements also show shifted *I*/*V* data consistent with upward band bending. Charge control of dangling bonds was accomplished through a distance relationship between the dangling bond and the $TiSi_2$ contact. The lowered chemical potential in the near contact region removes the ability of dangling bonds to become negatively charged while dangling bonds outside the close contact region remain fully charged. Methods to actively control dangling bond charge states are discussed.

KEYWORDS: scanning tunneling microscopy · dangling bonds · silicon · Schottky · titanium · silicide

The study of surface defects and, in particular, dangling bonds (DB) on semiconductor surfaces and at interfaces has been an area of interest for years. Interest was driven from the unique characteristics of the DB, due to fact that the DB state lies within the bandgap of the semiconductor. However, once deemed problematic, nanoscale science is now taking advantage of DBs for possible technological applications. For example, the creation, patterning, dynamics, and electronic properties of individual DBs, DB wires, and clusters have been discussed both experimentally and theoretically.[1−17] DB clusters have recently been shown to enter into a tunnel coupled relationship at close distances, providing applications in quantum cellular automata and as charge qubits.[18−20] The chemical reactions of DBs are also understood and allow templating of organic molecules on silicon surfaces.[21] As well, the charge of the DB (positive or negative) can selectively dictate the type of chemical reaction that occurs at the surface.[22] It has also been demonstrated that charged dangling bonds can control the flow of current through single molecules on silicon surfaces and the charge distribution in tunnel coupled DB systems.[18,23] Because the charge state of the DB can control the chemical and electronic properties of nanostructures, methods to control the charge state of a DB are desirable. One way to alter the DB charge state is through changing the dopant type or density. For example, highly doped n-type silicon ensures negative DBs, while minimally doped creates neutral DBs.[12,18,23] However, this method is impractical as it affords no active control over the DB charge state. Therefore, it is essential to develop a method to actively control the charge state of a dangling bond. In this manuscript, we propose and show that the charge state of a DB can be altered by using nanoscale Schottky contacts.

Schematically, the experiment is depicted in Figure 1. A nanoscale Schottky contact is created on the surface of hydrogen-terminated silicon. Because the hydrogen termination minimizes the number of surface states, the Fermi level is not pinned, and the bands are free to move under the potential influence of the contact. Therefore it is expected that band bending would be observed along the surface of the silicon, resulting in a depletion of electrons in the near surface region close to the contact. For highly doped n-type silicon, a local measure of the chemical potential in the vicinity of the contact predicts that the silicon close to the contact will image similar to low-doped silicon, while silicon at further distances from the contact will behave according to the bulk dopant density. It is therefore predicted that DBs that would normally appear negatively charged far from the contact would appear uncharged close to the contact. Electrically contacting the $TiSi_2$ islands and applying an external bias in order to alter the depletion region could be used to actively control the charge state of nearby

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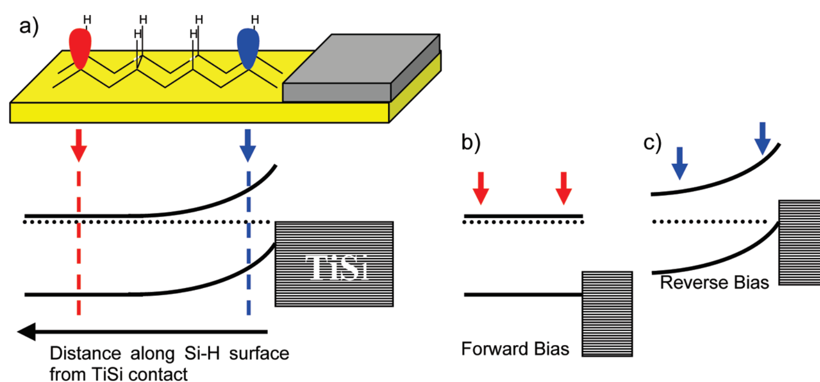


Figure 1. (a) Schematic representation of a Schottky contact on hydrogen-terminated silicon with nearby surface dangling bonds. Colors represent the charge state of the dangling bonds; red indicates negatively charged, and blue indicates uncharged. The charge state of the DB is dependent on the Fermi level. The band diagram illustrates the band bending along the silicon surface, from the titanium silicide contact, at equilibrium. The blue and red lines illustrate the chemical potential at distances from the Schottky contact. Blue: Fermi level is near the mid gap; DBs will appear uncharged. Red: Fermi level is near the conduction band; DBs will appear charged. (b) Schottky contact in forward bias. The bands are pulled down creating negatively charged DBs indicated with red arrows. (c) Schottky contact in reverse bias. The bands are pushed up creating uncharged DBs indicated with blue arrows.

DBs; reverse bias leading to the changing of negative DBs to neutral, and forward biases changing neutral DBs to negative. This charge control of individual DBs would help to realize proposed applications of quantum dot DB constructs and single-atom derived electronics.

Titanium adsorption and silicide formation on clean silicon surfaces have been studied using scanning tunneling microscopy (STM).[24−26] STM measurements of $TiSi_2$ island formation on Si(111) 7 × 7 and Si(100) 2 × 1 have shown that the $TiSi_2$ segregates into nanoscale islands. Both C49 and C54 phases have been observed and characterized. Barrier heights have been measured for titanium silicide islands on the order of 100 nm−1um sizes,[27] while islands of ∼5 nm diameter showed Coulomb blockade and Coulomb staircase effects at room temperature.[28] Patterned $TiSi_2$ microelectrodes have been prepared on Si(111) surfaces. It was shown that the patterned contacts survive momentary flashing to 1200 °C and do not contaminate the formation of Si(111) 7 × 7 between the microelectrode contacts.[29] Patterned $TiSi_2$ microelectrodes have also been shown to survive cleaning and NHF_4 etching conditions during the formation of hydrogen-terminated Si(111).[30]

In this report, we prepared $TiSi_2$ islands on ultrahigh vacuum (UHV) prepared hydrogen-terminated Si(100). The hydrogen-terminated surface offers several advantages compared to the previously studied clean surfaces, in that the surface is not reactive but more importantly the bands are not pinned and are free to bend under potential influence. We show that surface band bending at nanoscale titanium−silicon islands on hydrogen-terminated silicon is directly observed using the scanning tunneling microscope (STM). This band bending induced by the contact results in the depletion of electrons from the region close to the $TiSi_2$ islands. Dangling bonds that would normally be negatively charged far the $TiSi_2$ contact are found to exhibit a reduced charge state when observed within the depletion region.

RESULTS AND DISCUSSION

Figure 2 shows the sequence of steps to prepare the silicide islands on hydrogen-terminated silicon. Figure 2a shows the clean silicon surface of the Si(100) crystal relatively free of defects. Dimer rows, orthogonal to one another on alternating terraces, are visible under magnification. The steps between terraces are clearly visible. Figure 2b displays the as deposited titanium film from the thermal source. The steps of the silicon surface can still be observed. After annealing to 900 °C, the titanium film reacts with the silicon surface and forms islands of titanium silicide (Figure 2c). The size of the islands is dependent on the amount of titanium deposited and on the annealing temperature with higher coverages and temperatures leading to larger islands. The temperature used for the formation of the $TiSi_2$ islands is known to produce the C54 phase of the $TiSi_2$. The STM image in Figure 2d is equal to literature identifications of the C54(110) surface.

Figure 3 shows the surface after hydrogen termination. The effect of hydrogen termination of the silicon surface does not appear to alter the structure of the silicide islands (Figure 3a). Additionally, the silicide island does not affect the hydrogen termination process of the silicon surface as the hydrogen covered portions of the silicon surface appear identical to surfaces prepared with no silicide. For most experiments the hydrogen termination process occurred immediately after silicide formation.

Dangling bonds on the hydrogen-terminated surface image with dark surrounding halos are identical to samples prepared with no silicides (Figure 3b). The high Fermi level associated with the highly n-type doped hydrogen-terminated silicon causes the DB

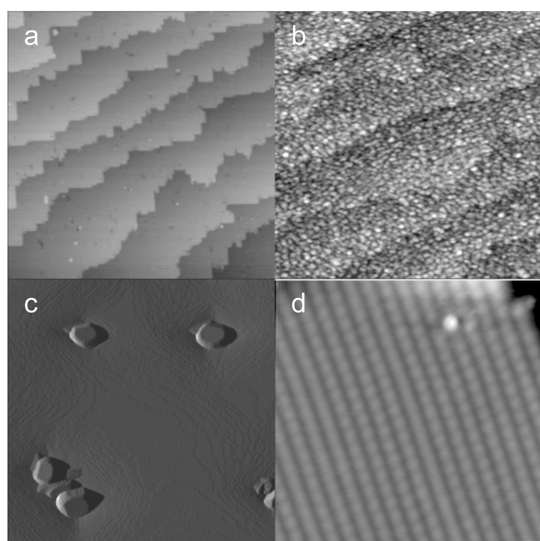
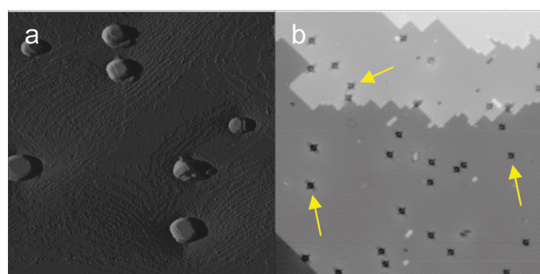


Figure 2. $TiSi_2$ formation: (a) 125 nm^2 STM image of the clean silicon surface prior to deposition of Ti and (b) 125 nm^2 STM image of the thermally deposited Ti. Steps are still observed. (c) $TiSi_2$ island formation after annealing the surface in image (b) to 900 °C (500 nm^2). (d) C54 phase of a TiSi island (12 nm^2).



c)

CBM

VBM

Figure 3. (a) Hydrogen termination of the surface does not affect the $TiSi_2$ structure; 125 nm^2 STM image shows that the $TiSi_2$ structures appear equivalent to those in Figure 1c. (b) Hydrogen-terminated silicon and dangling bonds on the surface appear normal in the STM image (50 nm^2). DBs appear negatively charge in accordance with the bulk dopant density used in the experiments (three are indicated with yellow arrows). (c) A band diagram representative of a negatively charged surface DB. Negative DBs are identified by a dark depression created by the upward band bending of the surrounding H−Si due to the negatively charged atom.

gap states to become occupied by one extra electron for a total of two electrons, rendering them negatively charged. The charged DBs bend bands upward, thereby locally inhibiting electron injection from the STM tip into the conduction band (CB) and causing a dark halo to surround DBs in unoccupied state images. A band diagram is shown in Figure 3c to schematically illustrate the local band bending induced by the charged DB

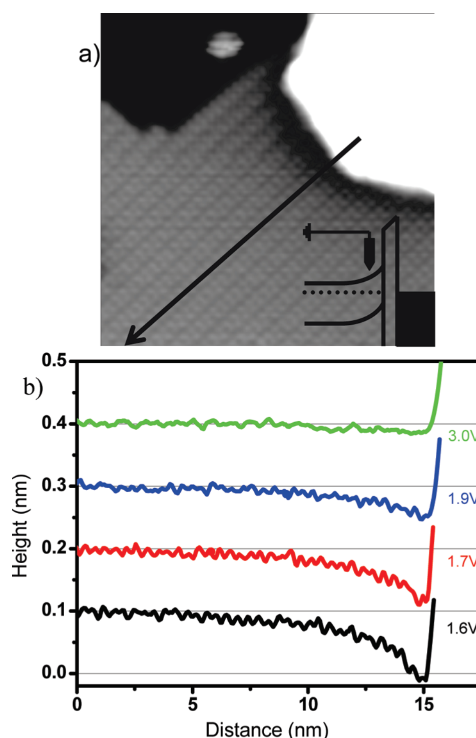


Figure 4. (a) STM image (1.6 V, 60 pA) of the hydrogen surface surrounding a small $TiSi_2$ island. The silicon surrounding the $TiSi_2$ appears darkened. The inset shows schematically the upward band bending and subsequent measurement of the depression surrounding the $TiSi_2$ island using empty state imaging. (b) Line profiles of the silicon surface collected at various voltages. Higher voltages reveal less depression in the silicon.

leading to the dark surrounding halo. The local band bending due to the charged DB is realized because the hydrogen termination process creates an unpinned surface with few defects. DB imaging is consistent regardless of whether they are created by single hydrogen atom removal with the STM tip or are naturally occurring, as a result of incomplete hydrogen termination.

Figure 4a shows an empty state STM image, acquired at 1.6 V, of a 14 nm radius $TiSi_2$ island on hydrogen-terminated Si(100) 2 × 1. It is quite clear that a depression is observed around the $TiSi_2$ island. The $TiSi_2$ island in the image is graphically saturated in order to emphasize the features of the silicon surface. The depression is not a result of a tip convolution from the 3 nm high $TiSi_2$ island, as this would lead to a brightening of the surface. This depression is a result of a decreasing ease of electron injection into the silicon surface with proximity to the $TiSi_2$ island. This is indicative of upward band bending and is analogous to the description of band bending associated with isolated DBs. The filled state images (−2 V, 0.1 nA) show almost no slope in the hydrogen surface and indicate that tip induced band bending obscures the local band bending induced by the $TiSi_2$ island.[31]

Line profiles for various empty state imaging biases are shown in Figure 4b. They show that the depth of

the observed depression is dependent on the imaging voltage with lower voltages showing the greatest depression and longest lateral range. The dependence of the depression depth and length with imaging voltage indicates that the tip-induced band bending of the hydrogen-terminated surface is competitive with the intrinsic band bending of the $TiSi_2$ island. At larger biases (>3 V), the slope is almost completely absent.

Figure 5 shows *I*—*V* spectra acquired at various distances from another TiSi island. The tip height was set using tunneling parameters of −2 V and 0.1 nA. The black *I*—*V* curve is an average of 10 individual spectra taken in close proximity to the TiSi island (~5 nm). The red *I*—*V* curve is an average of 10 individual spectroscopy curves acquired at an average distance of 15 nm to the $TiSi_2$ island. The green *I*—*V* curve is an average of 10 individual spectroscopy curves acquired at an average distance of 40 nm to the $TiSi_2$ island and is indicative of our measurement of the hydrogen-terminated silicon surface with no $TiSi_2$ islands.

The figures show that there is a shift of the *I*—*V* spectra. Current injection into the silicon from the tip becomes increasingly difficult as the tip is moved horizontally across the silicon surface toward the $TiSi_2$ island. This is consistent with an upward band bending of the silicon surface as schematically depicted in Figures 1 and 4. This shift is qualitatively similar to that seen in cross-sectional STM studies of cleaved silicon—gold systems.[31] These observations indicate that there is band bending observed along the surface, induced by the contact of the $TiSi_2$ island.

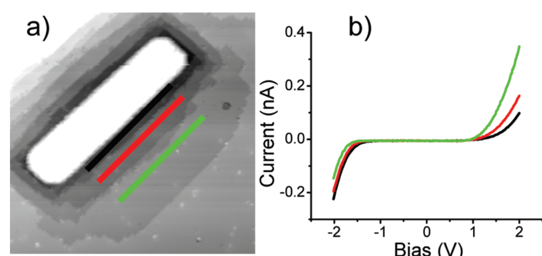


Figure 5. (a) STM image of a $TiSi_2$ island on hydrogen-terminated silicon. The black, red, and green bars indicate the regions where the corresponding spectra (b) were collected. Ten measurements were averaged for each of the three spectra. A shift of the *I*—*V* spectra is observed due to the surface band bending induced by the $TiSi_2$ island.

We have demonstrated that $TiSi_2$ islands induce band bending along the surface of hydrogen-terminated silicon. We now consider the effect that this band bending has on surface defects. It is known that the position of the Fermi level controls the charge state of the DB. For example, with n-type silicon samples, DBs are negatively charged when the dopant concentration is relatively high (>10^{17}cm^3) but appear neutral in charge when the dopant concentration is low.[18] Therefore, it is predicted that DBs that would normally appear negatively charged, based on the bulk doping density, should appear neutral in charge when created within the depletion region close to the $TiSi_2$ islands. STM imaging should be able to discern the charge state of the DBs using unoccupied state imaging; negatively charged DBs are observed to have a characteristic dark halo surrounding a small central spot, while uncharged dangling bonds appear as bright protrusions under the same imaging conditions.[12,18,19]

Figure 6a—c shows examples of STM images of DBs in close proximity to TiSi islands. The DBs close to the $TiSi_2$ island appear as bright protrusions, while those further from the island appear with halos. Note that the curving silicon surface representative of the band bending is observed in the STM images. Figure 6c shows a magnified region taken from Figure 6b along with a schematic representing the surface band bending of the silicon due to the $TiSi_2$ contact (from Figure 1). The image shows that there is a relationship between the charge state of the DB and the distance to the $TiSi_2$ contact; uncharged DBs are only observed close to the

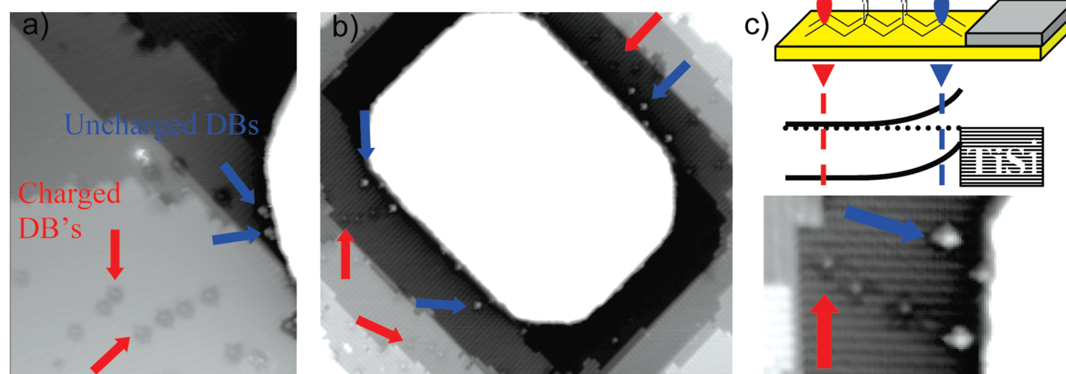


Figure 6. (a) A STM image showing dangling bonds at various distances from $TiSi_2$ islands. The $TiSi_2$ island is only partially shown as a saturated white feature. Dangling bonds appear as bright protrusions at close distances to the $TiSi_2$ islands, labeled with blue arrows. Dangling bonds at distances from the islands appear as negatively charged with dark depressions, labeled with red arrows. (b) Another experiment showing uncharged dangling bonds in close proximity to the $TiSi_2$ island. (c) Schematic representation of the $TiSi_2$-induced band bending creating uncharged DBs. The STM image is from a magnified region from (b) showing the distance dependence, from the $TiSi_2$ island, on the charge state of the DBs.

titanium silicide islands. It is, however, probable that each of the uncharged DBs become charged for a fractional time, based on the local Fermi level position resulting from the local band bending induced by the $TiSi_2$ contact, and that the experiments are performed at room temperature. This explains the very slight depression sometimes observed around the much brighter DB.[18,19] One might even expect the STM to observe a varying degree of time-averaged DB charging based on the distance of the DB to the $TiSi_2$ contact. However, this effect has not been observed with the STM imaging conditions of the current experiments and is likely due to the effect of tip-induced band bending as well as the electron tunneling dynamics. Future experiments including a full theoretical analysis of DB imaging will be provided elsewhere.

CONCLUSIONS

We have shown that bend bending around $TiSi_2$ islands is observed along the surface of hydrogen-terminated silicon. The lowered chemical potential in the near contact region alters the charge state of DBs, such that DBs that normally image as negatively charged based on the bulk doping density appear as uncharged DBs. In future work, we will work to establish a relationship describing the charge state of a DB as a function of distance to $TiSi_2$ islands. We will also explore the observed surface band bending and barrier. It is also anticipated that active control over the charge state of a DB can be achieved and observed using a multiple-probe STM by the application of a forward or reverse bias to the $TiSi_2$ islands.

METHODS

All STM images were collected with an Omicron VT-AFM/STM at room temperature in an UHV chamber with a base pressure of 6×10^{-11} Torr. The experiments were performed on n-type Si(100) 2×1 surfaces (As, 0.08 $\Omega \cdot$cm). The clean surface was prepared after outgassing of the sample at 600 °C for 12 h and flashing to 1250 °C. Titanium was then evaporated, using a thermal source, on to the clean surface held at room temperature. The surface was annealed to 900 °C for 30 s and then immediately cooled to 300 °C at which point the surface was hydrogen terminated by exposure (120 s) to atomic hydrogen created by a hot tungsten filament with a hydrogen pressure of 10^{-6} Torr.

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REFERENCES AND NOTES

1. Boland, J. J. Scanning Tunneling Microscopy Study of the Adsorption and Recombinative Desorption of Hydrogen from the Si(100)-2 × 1 Surface. *J. Vac. Sci. Technol., A* **1992,** *10*, 2458–2464.
2. Lyding, J. W.; Shen, T.-C.; Hubacek, J. S.; Tucker, J. R.; Abein, G. C. Nanoscale Patterning and Oxidation of H-Passivated Si(100)-2 × 1 Surfaces with an Ultrahigh Vacuum Acanning Tunneling Microscope. *Appl. Phys. Lett.* **1994,** *64*, 2010–2012.
3. Shen, T.-C.; Wang, C.; Abeln, G. C.; Tucker, J. R.; Lyding, J. W.; Avouris, Ph; Walkup, R. E. Atomic-Scale Desorption Through Electronic and Vibrational Excitation Mechanisms. *Science* **1995,** *268*, 1590–1592.
4. Shen, T.-C.; Avouris, P. Electron Stimulated Desorption Induced by the Scanning Tunneling Microscope. *Surf. Sci.* **1997,** *390*, 35–44.
5. McEllistrem, M.; Allgeier, M.; Boland, J. J. Dangling Bond Dynamics on the Silicon (100)2 × 1 Surface: Dissocation, Diffusion, and Recombination. *Science* **1998,** *279*, 545–548.
6. Foley, E. T.; Kam, A. F.; Lyding, J. W. Cryogenic UHV-STM Study of Hydrogen and Deuterium Desorption from Si-(100). *Phys. Rev. Lett.* **1998,** *80*, 1336–1339.
7. Stokbro, K.; Thirstrup, C.; Sakurai, M.; Quaade, U.; Hu, B.Y-K.; Perez-Murano, F.; Grey, F. STM-Induced Hydrogen Desorption Via a Hole Resonance. *Phys. Rev. Lett.* **1998,** *80*, 2618–2621.
8. Thirstrup, C.; Sakurai, M.; Stokbro, K.; Aono, M. Visible Light Emission from Atomic Scale Patterns Fabricated by the Scanning Tunneling Microscope. *Phys. Rev. Lett.* **1999,** *82*, 1241–1244.
9. Quaade, U. J.; Stokbro, K.; Thirstrup, C.; Grey, F. Mechanism of Single Atom Switch on Silicon. *Surf. Sci.* **1998,** *415*, L1037–L1045.
10. Hitosugi, T.; Heike, S.; Onogi, T.; Hashizume, T.; Watanabe, S.; Li, Z.-Q.; Ohno, K.; Kawazoe, Y.; Haswgawa, T.; Kitazawa, K. Jahn-Teller Distortion in Dangling-Bond Linear Chains Fabricated on a Hydrogen-Terminated Si(100)-2 × 1 Surface. *Phys. Rev. Lett.* **1999,** *82*, 4034–4037.
11. Bobrov, K.; Comtet, G.; Dujardin, G.; Hellner, L. Electronic Structure of Partially Hydrogenated Si(100)-(2 × 1) Surfaces Prepared by Thermal and Nonthermal Desorption. *Phys. Rev. Lett.* **2001,** *86*, 2633–2636.
12. Liu, L; Yu, J.; Lyding, J. W. Scanning Tunneling Microscopy Observation of Single Dangling Bonds on the Si(100)2 × 1:H Surface. *Mater. Res. Soc. Symp. Proc.* **2002,** *705*, Y6.6.1–Y6.6.6.
13. Soukiassian, L.; Mayne, A. J.; Carbone, M.; Dujardin, G. Atomic Wire Fabrication by STM Induced Hydrogen Desorption. *Surf. Sci.* **2003,** *528*, 121–126.
14. Soukiassian, L.; Mayne, A. J.; Carbone, M.; Dujardin, G. Atomic-Scale Desorption of H Atoms from the Si (100)-2 × 1:H Surface: Inelastic Electron Interactions. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2003,** *68*, 035303.
15. Abe, A.; Yamashita, K.; Saalfrank, P. STM and Laser-Driven Atom Switch: An Open-System Density-Matrix Study of H/Si(100). *Phys. Rev. B: Condens. Matter Mater. Phys.* **2003,** *67*, 235411.
16. Raza, H. Theoretical Study of Isolated Dangling Bonds, Dangling Bond Wires, and Dangling Bond Clusters on a H:Si(001)-(2 × 1) Surface. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2007,** *76*, 045308.
17. Dogel, I. A.; Dogel, S. A.; Pitters, J. L.; DiLabio, G. A.; Wolkow, R. A. Chemical Methods for the Hydrogen Termination of Silicon Dangling Bonds. *Chem. Phys. Lett.* **2007,** *448*, 237–242.
18. Haider, M. B.; Pitters, J. L.; DiLabio, G. A.; Livadaru, L.; Mutus, J. Y.; Wolkow, R. A. Controlled Coupling and Occupation of Silicon Atomic Quantum Dots at Room Temperature. *Phys. Rev. Lett.* **2009,** *102*, 046805.
19. Pitters, J. L., Livadaru, L., Haider, M. B., Wolkow, R. A. Tunnel Coupled Dangling Bond Structures on Hydrogen Terminated Silicon Surfaces. *J. Chem. Phys.*; accepted.
20. Livadaru, L.; Xue, P.; Shaterzadeh-Yazdi, Z.; DiLabio, G. A.; Mutus, J.; Pitters, J. L.; Sanders, B. C.; Wolkow., R. A. Dangling-Bond Dharge Qubit on a Silicon Surface. *New J. Phys.* **2010,** *12*, 083018.

21. Lopinski, G. P.; Wayner, D. D. M.; Wolkow, R. A. Self-Directed Growth of Molecular Nanostructures on Silicon. *Nature* **2000,** *406*, 48–51.
22. Dogel, S. A.; DiLabio, G. A.; Zikovsky, J.; Pitters, J. L.; Wolkow, R. A. Experimental and Theoretical Studies of Trimethylene Sulfide-Derived Nanostructures on p- and n-Type H-Silicon(100)-2 $\times$ 1. *J. Phys. Chem. C* **2007,** *111*, 11965–11969.
23. Piva, P. G.; DiLabio, G. A.; Pitters, J. L.; Zikovsky, J.; Rezeq, M.; Dogel, S. A.; Hofer, W. A.; Wolkow, R. A. Field Regulation of Single-Molecule Conductivity by a Charged Surface Atom. *Nature* **2005,** *435*, 658–661.
24. Bennett, P. A.; von Känel, H. Scanning Tunnelling Microscopy Studies of Silicides. *J. Phys. D: Appl. Phys.* **1999,** *32*, R71–R87.
25. Medeiros-Ribeiro, G.; Ohlberg, D. A. A.; Bowler, D. R.; Tanner, R. E.; Briggs, G. A. D.; Williams, S. R. Titanium Disilicide Nanostructures: Two Phases and Their Surfaces. *Surf. Sci.* **1999,** *431*, 116–127.
26. Briggs, G. A. D.; Basile, D. P.; Medeiros-Ribeiro, G.; Kamins, T. I.; Ohlberg, D. A. A.; Williams, S. R. The Incommensurate Nature of Epitaxial Titanium Disilicide Islands on Si(001). *Surf. Sci.* **2000,** *457*, 147–156.
27. Oh, J.; Nemanich, R. J. Current−Voltage and Imaging of $TiSi_2$ Islands on Si(001) Surfaces Using Conductive-Tip Atomic Force Microscopy. *J. Appl. Phys.* **2002,** *92*, 3326–3331.
28. Oh, J.; Meunier, V.; Ham, H.; Nemanich, R. J. Single Electron Tunneling of Nanoscale $TiSi_2$ Islands on Si. *J. Appl. Phys.* **2002,** *92*, 3332–3337.
29. Tong, X.; Wolkow, R. A. Scanning Tunneling Microscopy Characterization of Low-Profile Crystalline $TiSi_2$ Microelectrode on a Si(111) Surface. *Appl. Phys. Lett.* **2005,** *86*, 23101.
30. Palermo, V.; Buchanan, M.; Bezinger, A.; Wolkow, R. A. Lateral Diffusion of Titanium Disilicide as a Route to Contacting Hybrid Si/Organic Nanostructures. *Appl. Phys. Lett.* **2002,** *81*, 3636–3638.
31. Komeda, T.; Gwo, S.; Tokumoto, H. Cross-Sectional Scanning Tunneling Microscopy on Cleaved Si(111): Observation of Novel Reconstruction and Structural and Electrical Properties of MOS Interface. *Jpn. J. Appl. Phys.* **1996,** *35*, 3724–3729.