J. Phys. Chem. A **2007,** *111,* 12257−12259

Self-Directed Growth of Contiguous Perpendicular Molecular Lines on H−Si(100) Surfaces[†]

Janik Zikovsky,[‡] Stanislav A. Dogel,[‡] M. Baseer Haider,[‡] Gino A. DiLabio,[§] and Robert A. Wolkow*,[‡,§]

Department of Physics, University of Alberta, Edmonton, Alberta T6G 2G7, Canada, and National Institute for Nanotechnology, 11421 Saskatchewan Drive, Edmonton, Alberta T6G 2M9, Canada

Received: June 6, 2007; In Final Form: July 23, 2007

Future nanoscale integrated circuits will require the realization of interconnections using molecular-scale nanostructures; a practical fabrication scheme would need to be largely self-assembling and operate on a large number of like structures in parallel. The self-directed growth of organic molecules on hydrogen-terminated silicon(100) [H−Si(100)] offers a simple method of realizing one-dimensional molecular lines. In this work, we introduce the ability to change the growth direction and form more complex, contiguous shapes. Numerous styrene and trimethylene sulfide L shapes were grown on a H−Si(100)-3×1 surface in parallel with no intermediate surface lithography steps, and similar shapes were also grown using allyl mercaptan and benzaldehyde on H−Si(100)-2×1. Registered scanning tunneling microscopy (STM) images and high-resolution electron energy loss spectroscopy (HREELS) were used to investigate the growth process.

1. Introduction

Hybrid silicon−molecule nanoscale structures are of interest as a basis for future devices[1] because they have the potential to provide a stepping stone between well-established semiconductor manufacturing and fully molecular electronics. In order to become a viable technology, any such structures would need to be largely self-forming in a reproducible way. An ideal scheme would permit parallel growth of numerous similar structures, offer spatial and directional control, and allow for further functionalization or metallization to create molecular devices and their interconnects.

Several years ago, we described a promising process in which a chain reaction allowed the formation of self-directed linear structures of molecules on a hydrogen-terminated silicon surface.[2] This process requires a single silicon dangling bond (DB) as a starting point. The molecule bonds to this DB, leaving an unpaired electron on an atom in the molecule, which becomes passivated by abstracting a nearby hydrogen atom. The new DB thus created acts as a point for the next molecule to react, allowing the reaction to proceed in a chain and form ordered linear structures.

In the prototypical system for this process, styrene on H−Si(100)-2×1, molecules track substrate crystallinity by growing exclusively along dimer rows. Several other molecules have been found to grow in a similar fashion.[3−5] An effort to grow linear structures at a right angle to dimer rows used more flexible molecules that could “fit” the surface differently than styrene. Cyclopropyl methyl ketone[6] did indeed show different growth; however, the flexibility of that molecule permitted irregular growth, rather than restricting it to the perpendicular-to-row direction. It has also been shown that, on the relatively isotropic H−Si(111)-1×1 surface, irregular growth of styrene results.[7]

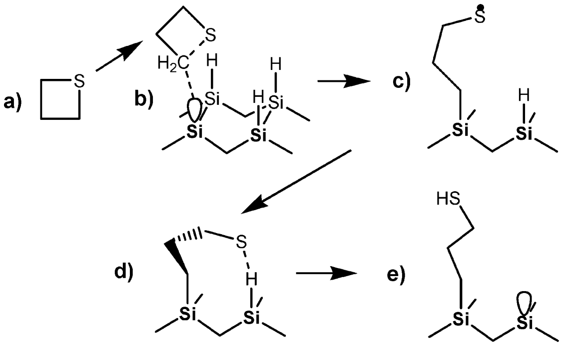

Figure 1. Proposed mechanism for line growth of TMS on dimer rows of H−Si(100)-3×1: (a) TMS approaches the surface. (b) The ring breaks, and a C−Si bond is formed simultaneously. (c) A S-centered radical is left. (d) The S-centered radical abstracts H from an adjacent dimer. (e) The attached molecule ends in S−H, and a new DB on the next dimer is present to continue line growth.

More progress was made when cross-dimer row growth was found for styrene on the H−Si(100)-3×1 surface.[8] Further work by Hossain et al.[9] showed that allyl mercaptan exclusively formed cross-dimer row lines on 2 × 1. In subsequent work,[10] an effort was made, but without success, to grow contiguous lines of allyl mercaptan and styrene that would have resulted in a molecular line turning at a right angle, creating an “L shape”. Such structures were obtained, but only after using the STM tip to create a dangling bond for use as the starting point of the second line.

In this work, using still different chemistry, contiguous heteromolecular lines with a change in growth direction were achieved by simply halting the dose of one molecule and then dosing a second species. Primarily, we used the H−Si(100)-3×1 surface, initiating lines across dimer rows by dosing styrene and continuing them along rows by subsequently dosing trimethylene sulfide (TMS). In contrast to earlier work, because the L shapes created did not require any intermediate steps of nanolithography, a large number of like structures were formed in parallel on the Si substrate.

[†] Part of the “Giacinto Scoles Festschrift”.

* To whom correspondence should be addressed. E-mail: rwolkow@ualberta.ca.

[‡] University of Alberta.

[§] National Institute for Nanotechnology.

10.1021/jp074389p CCC: $37.00

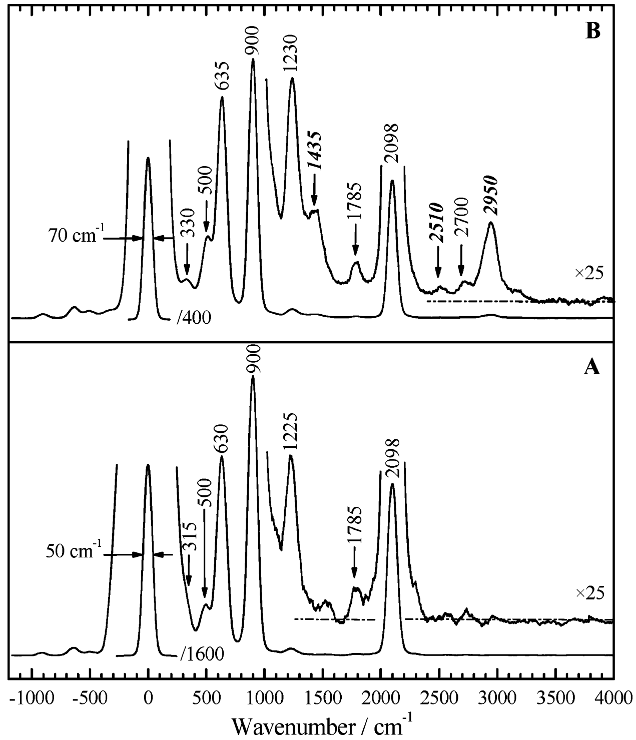

Figure 2. HREEL spectra of H$-$Si(100)-3$\times$1 (A) before and (B) after 100 L dose of trimethylene sulfide. For peak assignment of the H$-$Si(100)-3$\times$1 surface spectrum shown in spectrum A, see ref 17. The molecular vibrations in spectrum B that are clearly distinguishable from those of SiH and SiH$_2$ species are highlighted: 1435 cm^{-1}, scissor of CH$_2$; 2510 cm^{-1}, S$-$H stretch; and 2950 cm^{-1}, symmetric and asymmetric stretches of CH$_2$.[18] Other expected vibrations such as Si$-$C, C$-$C, and some CH$_2$ modes are observed indirectly through the shifting and broadening of peaks. As in ref 12, we were unable to assign a molecular vibration to the peak around 2700 cm^{-1}. The presence of the 2510 cm^{-1} S$-$H stretch peak supports our proposed attachment geometry of trimethylene sulfide bonding through a carbon to n-type silicon.[12]

2. Experimental Methods

The experiments described herein were conducted in an ultrahigh-vacuum system (pressure below 10^{-10} Torr) equipped with a scanning tunneling microscope (Omicron STM 1) and a high-resolution electron energy loss spectrometer (HREELS, LK 3000), allowing us to use both instruments without taking samples out of vacuum. The As-doped (0.08$-$0.1 Ω·cm) Si(100) substrates were degassed overnight at 870 K by direct current heating and then flashed repeatedly to 1520 K for 5 s to remove the native oxide. Under a pressure of 10^{-6} Torr of atomic hydrogen cracked by a hot tungsten filament, the crystal was flashed to 1520 K and then allowed to cool. During the 4-min H exposure, the position of the crystal in front of the filament was adjusted so that a thermocouple placed close to the sample holder would read from 373 to 393 K, resulting in the desired 3 × 1 termination of the Si(100) surface. This surface consists of alternating parallel rows of dihydride monomers (with two H on one Si) and Si dimers (single H per Si), which appear higher in STM than the monomer rows.[11] A temperature of 593 K during H exposure was used to obtain a 2 × 1 surface.

Growth of molecular lines was performed by introducing specific molecules into the vacuum chamber in the gas phase. The molecules used in this study (styrene, trimethylene sulfide, allyl mercaptan, and benzaldehyde) were subjected to several freeze$-$pump$-$thaw cycles prior to dosing on a room-temperature substrate in situ in the STM chamber through a variable leak valve (1 L = 1 s at 10^{-6} Torr, uncorrected ion-gauge reading).

3. Results and Discussion

3.1. HREELS Results. Growth of TMS on the H$-$Si(100)-3$\times$1 surface occurs with the simultaneous breaking of the ring at the C$-$S bond and the formation of a C$-$Si bond with the surface, as shown schematically in Figure 1. The sulfur radical on the other end of the molecule then abstracts hydrogen from a nearby dimer, creating a new DB where growth can continue. To confirm this growth process, HREELS measurements were performed on samples exposed to a 100 L dose of TMS (see Figure 2). The presence of a peak at 2510 cm^{-1}, corresponding to the S$-$H stretch, indicates that, on H$-$Si(100)-3$\times$1, TMS attaches through the carbon atom. This result is expected on an n-type Si(100) crystal.[12]

3.2. STM Results. Whereas TMS forms double lines on H$-$Si(100)-2$\times$1, with growth occurring in a square-wave pattern on two adjacent dimer rows,[12] on the 3 × 1 surface, growth is restricted to only the dimer row. We did not observe TMS lines crossing monomer rows. Indeed, theoretical calculations[13] indicate that the barrier is 2.3 kcal/mol higher for abstraction from the monomer site than for abstraction from the next dimer site. This indicates that monomer row crossings for TMS should occur in only 0.1% of growth events.

Figure 3 shows the parallel growth of several L-shaped molecular nanostructures starting at randomly placed DBs. First,

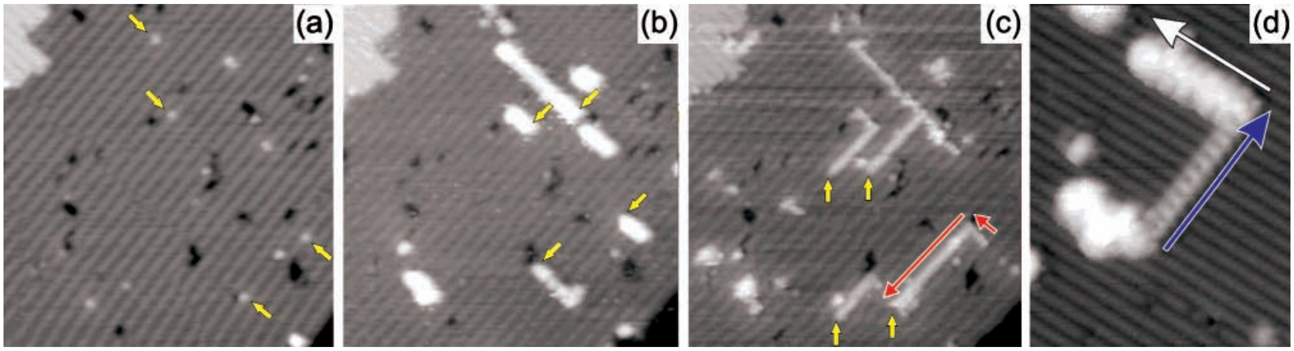

Figure 3. Sequence of STM images (30 × 30 nm) showing growth of several contiguous, L-shaped molecular lines. Images a$-$c are of the same area of the surface. (a) Initial 3 × 1 H-terminated surface (0.08 nA, $-$2.8 V), showing the DBs several of which will react. (b) Following a 50 L dose of styrene (0.08 nA, $-$2.8 V), several styrene lines have grown perpendicular to dimer rows. (c) Following a 140 L dose of TMS (0.12 nA, $-$3.4 V), a few contiguous L-shaped molecular lines of styrene followed by TMS have formed. The yellow arrows indicate the DB positions and the direction of subsequent line growth; the red arrows trace the growth of one structure. (d) L shape of allyl mercaptan (blue arrow) followed by benzaldehyde (white arrow) on H$-$Si(100)-2$\times$1 (12 × 15 nm, 0.08 mA, $-$1.8 V).

several STM images of the 3 × 1 H-terminated surface were acquired (Figure 3a) in order to locate the starting DB positions, as indicated by yellow arrows. The STM tip was then retracted by several microns so as not to inhibit gas-borne molecules reaching the surface, and the sample was exposed to 50 L of styrene. Figure 3b shows the same area, now with lines of styrene molecules perpendicular to dimer rows.[14] The growth process moved the DBs to the end of the styrene lines, indicated by arrows. Finally, Figure 3c shows the same area after a 140 L dose of TMS: several L-shaped nanostructures were formed. The red arrows in Figure 3c trace the growth process for one particular molecular line: TMS lines grew from the DB at the end of the styrene lines, but followed the dimer row direction. The yellow arrows indicate where line growth stopped, as a result of either a limited TMS supply, surface defects, or possibly self-termination of the line growth process.

Demonstrating that this process is not exclusive to this surface or these compounds, Figure 3d shows an L shape formed on H−Si(100)-2×1 with different compounds: 100 L of allyl mercaptan (blue arrow) followed by 75 L of benzaldehyde (white arrow). The independent growth of these two molecules on H−Si(100)-2×1 has been shown previously;[5,10,11] we show here that they can form contiguous L shapes when dosed in sequence. These shapes grew less frequently than TMS and styrene L shapes, but we were able to image them at a higher resolution.

Similar shapes obtained previously[10] required the extra step of creating a new DB in a particular position where growth at a right angle was desired. In both systems shown here, no scanned-probe intervention is necessary; therefore, growth of these L shapes occurs over the entire Si surface simultaneously, creating the potential for broadly parallel fabrication.

Growth of TMS following styrene occurs with a fairly high probability; the reverse, growth of styrene following TMS, is rarer. We have been unable to confirm further contiguous growth of an L-shaped feature to create, for example, a U shape or other more complex structures. The length of molecular lines grown in this method is ultimately controlled by the amount of gas dosed into the chamber; however, we note that, even though the dose was identical for the entire surface, the length of the lines formed was not uniform. Let us also remark that the required doses for both molecules were comparatively higher than those for, as an example, styrene growing on H−Si(100)-2×1. Finally, we note that, in this system, we cannot control whether perpendicular TMS growth will continue to the right or the left of the styrene line. However, the inclusion of chiral centers or the application of an electric field might allow us to gain this final degree of control.[15,16]

4. Conclusions

In summary, we have shown the first contiguous growth of composite molecular lines where the ability to change growth direction was obtained by the simple turn of a valve. A large number of similar nanostructures were formed in parallel on a macroscopic sample without the need for labor-intensive intermediate lithographic steps. These structures are appealing because of the possibility of further functionalization allowing them to act as molecular-scale active devices or passive interconnects. We presently lack a sufficiently detailed understanding of the growth process to achieve highly regular growth and to explain why particular molecules fail to follow certain other pre-existing molecules on the surface. However, we have demonstrated evolving design principles for hybrid Si−molecular structures. Likely, the puzzles now limiting fuller control will yield to further study and will enable simultaneous growth of many like structures through very simple means. Such structures might enable future hybrid silicon−molecular integrated circuits.

Acknowledgment. We thank NSERC and iCORE for funding.

References and Notes

(1) Wolkow, R. A. *Ann. Rev. Phys. Chem.* **1999**, *50*, 413−441.

(2) Lopinski, G. P.; Wayner, D. D. M.; Wolkow, R. A. *Nature* **2000**, *406* (6791), 48−51.

(3) Kruse, P.; Johnson, E. R.; DiLabio, G. A.; Wolkow, R. A. *Nano Lett.* **2002**, *2* (8), 807−810.

(4) Basu, R.; Guisinger, N. P.; Greene, M. E.; Hersam, M. C. *Appl. Phys. Lett.* **2004**, *85* (13), 2619−2621.

(5) Pitters, J. L.; Dogel, I.; DiLabio, G. A.; Wolkow, R. A. *J. Phys. Chem. B* **2006**, *110* (5), 2159−2163.

(6) Tong, X.; DiLabio, G. A.; Clarkin, O. J.; Wolkow, R. A. *Nano Lett.* **2004**, *4* (2), 357−360.

(7) Cicero, R. L.; Chidsey, C. E. D.; Lopinski, G. P.; Wayner, D. D. M.; Wolkow, R. A. *Langmuir* **2002**, *18* (2), 305−307.

(8) Tong, X.; DiLabio, G. A.; Wolkow, R. A. *Nano Lett.* **2004**, *4* (5), 979−983.

(9) Hossain, Z.; Kato, H. S.; Kawai, M. *J. Am. Chem. Soc.* **2005**, *127* (43), 15030−15031.

(10) Hossain, M. Z.; Kato, H. S.; Kawai, M. *J. Phys. Chem. B* **2005**, *109* (49), 23129−23133.

(11) Boland, J. J. *Adv. Phys.* **1993**, *42* (2), 129−171.

(12) Dogel, S. A.; DiLabio, G. A.; Zikovsky, J.; Pitters, J. L.; Wolkow, R. A. *J. Phys. Chem. C* **2007**, *111*, 11965−11969.

(13) The calculation method employed is the same as that described in ref 12.

(14) The styrene growth on 3 × 1 in ref 7 showed wider spacing, because the multiple small doses used gave sufficient time for a DB to hop from the monomer to the next dimer. This does not occur for a single large dose, where growth occurs on both the dimer and the monomer.

(15) Lopinski, G. P.; Moffatt, D. J.; Wayner, D. D.; Wolkow, R. A. *Nature* **1998**, *392* (6679), 909−911.

(16) Lopinski, G. P.; Moffatt, D. J.; Wayner, D. D. M.; Zgierski, M. Z.; Wolkow, R. A. *J. Am. Chem. Soc.* **1999**, *121* (18), 4532−4533.

(17) Angot, T.; Bolmont, D.; Koulmann, J. J. *Surf. Sci.* **1996**, *352*, 401−406.

(18) Bellamy, L. J., *The Infra-red Spectra of Complex Molecules*, 3rd ed.; Chapman and Hall: London, 1975; p 433.