Fabrication of Interconnected 1D Molecular Lines along and across the Dimer Rows on the Si(100)−(2 × 1)−H Surface through the Radical Chain Reaction

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To realize nanoscale wiring in two dimensions (2D), the fabrication of interconnected one-dimensional (1D) molecular lines through the radical chain reaction of alkene molecules (CH_2=CH−R) on the H-terminated Si(100)−(2 × 1) surface have been investigated using scanning tunneling microscopy (STM) at 300 K. By the judicious choice of R in the CH_2=CH−R molecule and by creating a dangling bond (DB) at a desired point using the STM tip, the perpendicularly connected allyl mercaptan (ALM) and styrene lines have been fabricated on the Si(100)−(2 × 1)−H surface. The continuous growth of the styrene line at the end DB of a growing ALM line (or vice versa) does not occur, perhaps, due to steric hindrance or/and interaction between adsorbed molecules.

Organic molecules on the surface have the potential to be used as a basic component of electronic devices as well as a connecting wire in nanoscale electronic devices.[1,2] Wiring of the single molecule devices into a circuit is one of the key requirements for realization of molecule-based electronics. The silicon surface is considered to be the most promising alternative substrate for molecular electronics because of its compatibility with organic molecules, semiconductor band structure, and existing microelectronics.[3,4] Among a variety of techniques for the fabrication of a one−dimensional (1D) line of metal atoms or molecules on various surfaces,[5−7] the dangling bond (DB) initiated radical chain reaction on the H-terminated Si(100)−(2 × 1) surface has the particular advantage of allowing rapid fabrication of molecular lines with predefined position, length, composition, and structure. The recent breakthrough in the electronic properties of 1D molecular lines along the dimer rows on the Si(100)−(2 × 1)−H surface opens a new possibility of using such a 1D molecular line as a connecting wire in the organic−silicon hybrid devices.[8] In addition to the electron transport phenomenon through the molecular line, molecular line junctions might show the properties of gating, switching, sensing, and transistor function.[2,3,8] Since the Si(100)−(2 × 1)−H surface is anisotropic, control over the growth direction (along or across the dimer rows) is essential to fabricate interconnected 1D molecular lines that can connect two predefined positions on the 2D surface. Until recently, there was difficulty in growing the molecular lines across the dimer rows through chain reaction, because the surface periodicity across the dimer rows (7.68 Å) is twice the length of that along the dimer rows (3.84 Å). Our recent findings suggest that the growth of the 1D molecular line can be directed not only along

but also across the dimer rows on Si(100)−(2 × 1)−H by selecting the appropriate molecular systems.[9]

It has been known that some molecules containing an alkene moiety (CH_2=CH−R) undergo radical chain reaction on the H-terminated silicon surface.[7−13] The proposed reaction mechanism for chain reaction along and across the dimer rows is schematically shown in Figure 1a−f.[7,9,14] The first step of reaction involves the interaction of >C=C< with an unpaired dangling bond (DB) on the surface, which results in the creation of a C (carbon)-centered radical as shown in Figure 1a,b. The stability of the C-centered radical (Figure 1b) is thought to be the key for the successful growth of molecular lines.[12,15] To date, styrene (CH_2=CH−Ph),[7,13] vinyl ferrocene,[10] long-chain alkenes (C_nH_{2n}; $n \geq 8$),[12] and allyl mercaptan (CH_2=CH−CH_2−SH)[9] have been found to undergo chain reaction, while propylene (CH_2=CH−CH_3), 1-heptene, vinyl cyclohaxane, 4-vinyl pyridine, and allyl methyl sulfide (CH_2=CH−CH_2−S−CH_3) do not show any line growth. We found that the direction (along or across the rows) of chain reaction depends on the chemical constituent of R. When R is Ph, ferrocene, or C_nH_{2n+1} ($n \geq 6$), the molecular line grows along the dimer rows, as shown in Figure 1g. In contrast, when R is CH_2−SH, the line grows across the rows as shown in Figure 1h. We deduce that the distance of the intermediate radical site from the anchoring point of the molecule plays an important role in determining the growth direction.[9] In addition, some other effects such as steric effect between the substrate atoms and the adsorbed molecule may also contribute in determining the growth direction. When R is Ph, ferrocene, or C_nH_{2n+1} ($n \geq 6$), the intermediate C-centered radical can reach the nearest H (3.8 Å apart) within the same row to abstract it, and thus create a new radical on the next dimer in the same rows as shown in Figure 1c.[12] The new radical of Figure 1c is now ready to accept another molecule leading to the reaction along the dimer rows. In contrast, when R is CH_2−SH, the C−centered radical is

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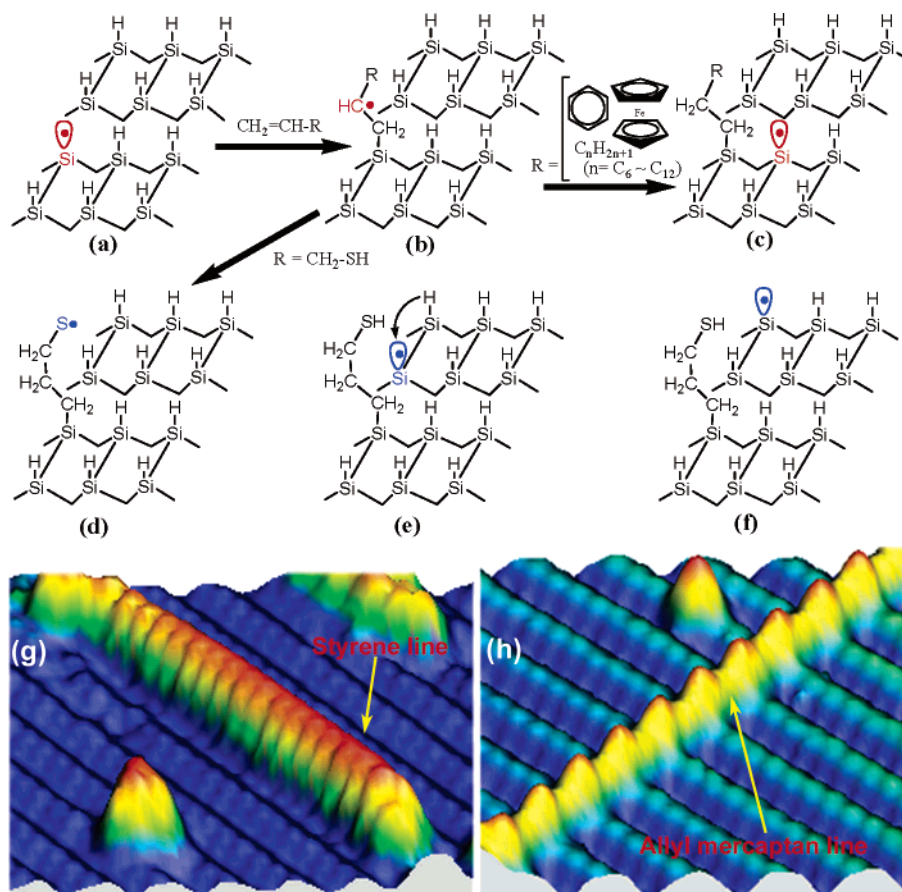† RIKEN.
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Figure 1. (a−f) Schematic of the mechanism of radical chain reactions along and across the dimer rows on the H-terminated Si(100)−(2 × 1) surface. (g,h) STM images of molecular lines running along and across the dimer rows. For (g), $V_{sample} = -1.1$ V, $I = 0.2$ nA, scan area = 9.2 × 6.3 nm^2; and for (h), $V_{sample} = -1.8$ V, $I = 0.2$ nA, scan area = 7.0 × 5.5 nm^2.

believed to undergo tautomerism and results in a thiyl radical as shown in Figure 1d.[16,17] It seems that the distance of the S (sulfur) radical from the anchoring site (∼5 Å) is appropriate to reach the H atom (∼5.1 Å apart) on neighboring row and abstract it. The abstraction of H from the neighboring row (perhaps followed by intradimer DB diffusion, Figure 1e) results in a DB site on the next rows (Figure 1f), which can now accept another molecule leading to the cross-row chain reaction. Thus, with variant R in CH$_2$=CH−R molecules, the chain reaction can be directed along or across the dimer rows on the Si(100)−(2 × 1)−H surface. In this letter, we report the fabrication of interconnected cross-row allyl mercaptan and parallel-row styrene lines on the Si(100)−(2 × 1)−H surface through DB-initiated radical chain reaction and evaluates its potential for 2D wiring in future molecular devices.

The experiments were performed in ultrahigh vacuum (UHV) condition with base pressure better than 1×10^{-10} mbar at room temperature. A variable-temperature scanning tunneling microscope (Omicron VT-STM) was used. The B-doped silicon sample was cleaned by prolonged annealing at ∼850 K (∼8 h) followed by repeated flashing at 1400 K. The clean surface was made H-terminated at ∼625 K by exposing to atomic H generated by a hot W filament (∼2100 K). The freshly prepared H-terminated surface usually contains a dilute concentration of unpaired DBs resulting from the incomplete H-termination;[18] otherwise, a DB at a predefined position is generated using the STM tip.[19] Chemicals including styrene, allyl mercaptan (ALM), and 2,4-dimethylstyrene (DMS) purchased from Aldrich were purified by several freeze−pump−thaw cycles . The amounts of molecule dosed are expressed in Langmuir (1 L = 1×10^{-6}

Torr·s), which is estimated by the background pressure during the exposure.

Figure 2a shows an STM image of the Si(100)−(2 × 1)−H surface, containing a dilute concentration of DBs, exposed to ∼5 L of ALM at 300 K. Two line structures of unequal lengths, running perpendicular to the dimer rows, are the assemblies of adsorbed ALM molecules (ALM lines) resulting from a chain reaction initiated at an unpaired DB.[9] These ALM lines remain unchanged even at 650 K, which ensures that the ALM molecules are chemically bonded to the silicon substrate. Each protrusion in the ALM line indicates an adsorbed ALM molecule, and it is located on individual dimer row, i.e., the distance between two successive protrusions is 7.68 Å. The irregularly shaped bright protrusions may be the styrene molecule adsorbed on the defect sites. Note that, similar to the growth of styrene line, the ALM line can also be grown from the DB site created by the STM tip.[9]

Since there are several molecules which undergo the chain reaction along the dimer rows, it should be possible to connect those ALM lines through a molecular line by initiating a chain reaction at a desired position on the rows that touched both ALM lines. We attempted to create a single DB at the position shown in Figure 2a using high-voltage pulse injection from the STM tip. The bright protrusion indicated by "DB" in Figure 2b may be the unpaired DB or a styrene molecule (from the background) already reacted with the freshly created DB. When the surface shown by Figure 2b is exposed to ∼5 L of styrene, a bright line connecting both the ALM lines appeared (Figure 2c). This new bright line is ascribed to the styrene line. The part of the styrene line indicated by "D" is a double line, which
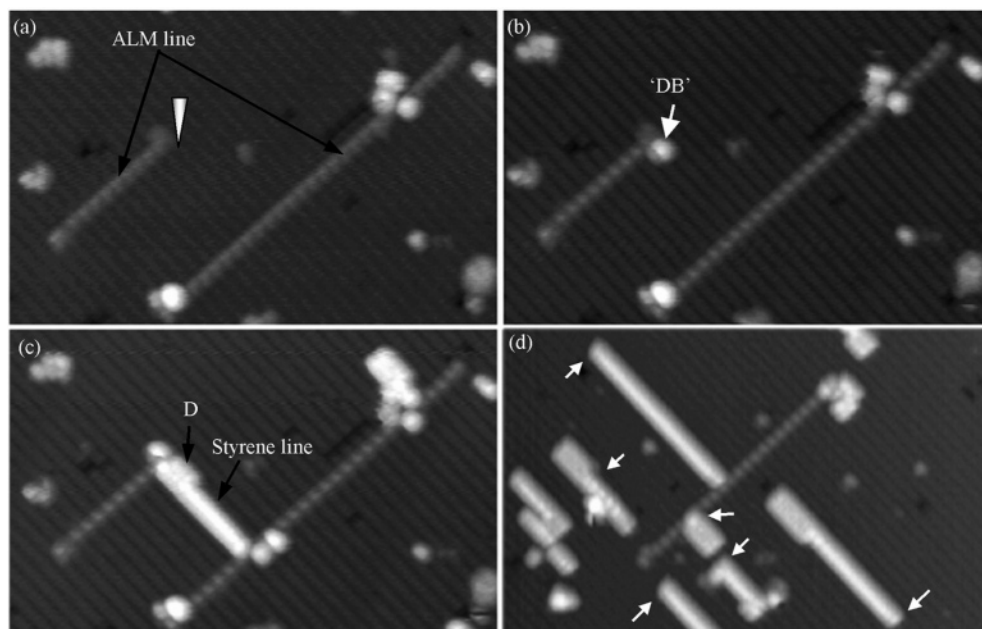
Figure 2. Selected area STM images of (a) the Si(100)−(2 × 1)−H surface containing two allyl mercaptan (ALM) lines, (b) a dangling bond (DB) created using STM tip at the position shown in (a), and (c) the surface (b) is exposed to ~5 L of styrene at room temperature. (d) The Si(100)−(2 × 1)−H surface containing an ALM line is exposed to 10 L of styrene after creating several DBs at the position indicated by arrows. $V_{sample} = -2.6$ V; $I = 0.2$ nA. Scan areas: (a−c) 26 × 16 nm^2 and (d) 32 × 20 nm^2.

is a common phenomenon in the case of styrene line growth.[7] In addition, a short double line and two individual protrusions aligned at the edge of the longer ALM line are observed as shown in Figure 2c. Sometimes, such protrusions at the edge of the ALM line are observed, but the length is always limited to ~2−4 protrusions even after large exposure to the styrene molecule. It is not clear whether these protrusions are the styrene molecules weakly bound with the ALM line or chemically bonded to the silicon substrate. The unequal contrast of the ALM and styrene lines may be due to the difference in topographic heights of the adsorbed molecules. The adsorbed styrene molecules are found to be standing up on the surface,[7,11] whereas the ALM molecule are expected to be tilted to the line growth direction.[9]

To grow a styrene line that perpendicularly connects a preexisting ALM line, it is not essential to create DB adjacent to the ALM line as done in Figure 2a. The styrene line initiated at a DB in a clean terrace can grow on either side of the DB site along the dimer rows, i.e., the C-centered radical in Figure 1b can abstract H either from the right-side dimer (Figure 1c) or the left-side dimer. These suggest that, if a DB is created even a little away from the ALM line, the growth of the styrene line initiated at that DB site could be directed toward the ALM line or away from it. Figure 2d shows such growths of styrene lines initiated by the DB sites located at different distances from an ALM line, in which, arrows indicate the location of DB sites on the initial surface. It is observed that some of the styrene lines have grown toward the ALM line and ultimately connected with it, while others have grown away from the ALM line. Alternatively to the line growth shown in Figure 2, the growth of an ALM line to connect a preexisting styrene line at a desired location has also been achieved (Supporting Information, Figure S1). These observations suggest that the perpendicularly connected molecular lines of styrene and ALM can be fabricated at a desired location by generating the DB site at the appropriate position.

It is observed that the styrene line never crosses over the ALM line on its way to growth, i.e., the styrene line initiated at the

DB on a dimer adjacent to the ALM line is directed away from ALM line, and the line initiated at the DB site a little farther but directed toward the ALM line is always stopped at the edge of the ALM line. These observations suggest that the intermediate radical (Figure 1b) of the styrene molecule anchored on the dimer adjacent to the ALM line could not abstract the H from the dimer, which lies along the ALM line. In such a case, there should exist an intermediate radical at the end of the styrene line stopped by the ALM line. This intermediate radical can either lead the styrene line growth in the backward direction to form a double line, as is returned by a missing dimer defect on its way to growth (Figure 2d), or reverse the chain reaction to desorb the styrene molecules ("unzipping event").[7] In the present study, a double line resulting from the obstruction of the ALM line on its way to growth has not been observed. In most cases, the interconnected styrene line is found to be stable. In rare events, some reverse reaction is observed after a few tens of minutes scanning at 300 K. Thus, we suggest that the end intermediate radical adjacent to the ALM line is stabilized by the interaction with the adsorbed ALM.

In a brief survey with different molecules, we observed that DMS reacts with the DB on the Si(100)−(2 × 1)−H surface similarly to styrene; however, many other molecules such as allyl methyl sulfide, ethylene sulfide, 5-bromo-1-pentene, acrylic acid, and 4-vinylpyridine do not show any line growth. Figure 3a shows two DMS lines on the Si(100)−(2 × 1)−H surface grown by exposure of ~5 L of DMS molecules. Hence, instead of styrene, DMS can also be used to make interconnected molecular lines. A simple perpendicular junction between ALM and DMS lines are shown in Figure S2 (Supporting Information).

It is noted that there exists a DB site at the end of molecular line ("growing line") where the line growth has not yet been terminated by a preexisting DB, defect, or other.[7,9] Hence, instead of creating a new DB at the vicinity of the ALM line, the end DB site of a growing line (for example, ALM line) should also be able to initiate a line growth along the rows if the surface is exposed to styrene or DMS. Here, we attempted to grow a DMS line at the end of the ALM growing line as
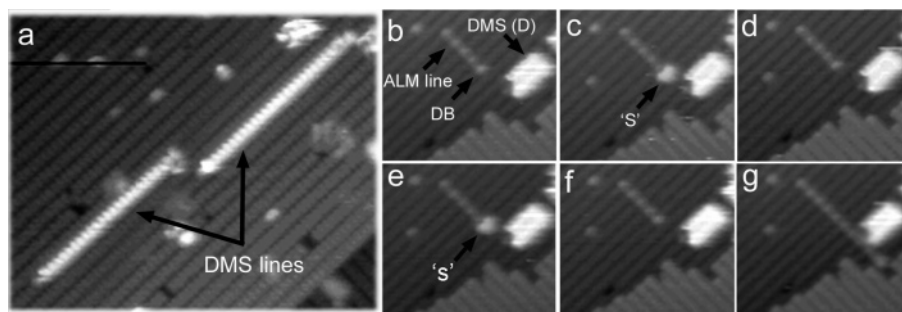
Figure 3. Selected area STM images of Si(100)−(2 × 1)−H surface showing (a) two 2,4-dimethylstyrene (DMS) lines, (b) a growing allyl mercaptan line (ALM) with an end dangling bond (DB) site and a nearby DMS double line, (c) (b) exposed to 5 L of DMS, (d) 6 min after (c), (e) (d) exposed to 7 L of DMS, (f) 6 min after (e), and (g) (f) exposed to 0.5 L of ALM. $V_{sample} = -2.5$ V; $I = 0.2$ nA. Scan areas: (a) 17 × 14 nm^2 and (b−g) 11.2 × 9.6 nm^2.

shown in Figure 3b−g. A growing ALM line with an end DB site is shown in Figure 3b, where a double DMS line is also seen. After exposure of ∼5 L of DMS (Figure 3c), which was enough to grow DMS lines at the isolated DB site with significant lengths, no DMS line is observed at the end DB site. Instead, a protrusion (indicated by "s") much brighter than an ALM line is observed at the DB site (Figure 3c). Surprisingly, the bright protrusion disappeared in the image (Figure 3d) scanned after 3 min of Figure 3c. In the repeated attempt on the surface shown in Figure 3d, the similar phenomena of appearance and disappearance of the protrusion ("s") are observed as shown in Figure 3e and f, respectively. To confirm that there is a DB site at the end of the ALM line, the surface shown in Figure 3f was exposed to ∼0.5 L of ALM molecules. The ALM line is found to extend up to the edge of the terrace as shown in Figure 3g. This clearly shows the presence of a DB site at the end of the growing ALM line. These observations suggest that adsorbed DMS molecule (possibly the radical as shown in Figure 1b) cannot abstract H from the neighboring dimer in the row to initiate a chain reaction but desorbs, leaving an intact DB site. A similar attempt was also made for styrene to grow a line from the end of a growing ALM line, but the growth was not successful as well. These may relate to the steric hindrance between adsorbed styrene and ALM molecules, to attain the configuration suitable for abstraction of H from the nearest dimer rows. However, the other possibility of stabilization of the DMS intermediate radical by interaction with the adsorbed ALM cannot be ruled out completely.

It has been reported that some DBs show much faster growth of molecular lines than others, while some DBs show no growth at all.[7] Although the statistical details and reaction dynamics are not available yet, in addition to the proposed autocatalytic effect,[7] some other factors such as activation barrier for desorption, DB diffusion, and (or) steric hindrance for a molecule to reach the DB site may also contribute to the observed phenomena of unequal growth of molecular lines. We found that the probability of formation of a styrene line on a DB site is higher than that of ALM, which may be related to the activation barrier for intradimer DB diffusion as shown in Figure 1e. On the basis of the results of temperature and time dependence measurements, the stability of an ALM line was found to be much higher than that of a styrene line. The forthcoming studies with different molecular systems and substrate temperatures will explore the suitable conditions for extended complex connections of molecular lines on the Si-(100)−(2 × 1)−H surface.

Unlike a styrene line, the as-prepared ALM line might not show any field-regulation conduction effect.[8] However, the ALM line possesses free −SH groups in the vacuum side, which is expected to be reactive toward various metal atoms as well as many biological molecules. Since the H-terminated Si(100)−(2 × 1) surface is less reactive toward many metal atoms, the interconnected molecular line shown in the present study has the potential to be used as a template to fabricate nanowires on the preselected location by attaching metal atoms with the molecular lines.

In conclusion, the fabrication of interconnected 1D molecular lines on the Si(100)−(2 × 1)−H surface has been investigated using scanning tunneling microscopy (STM) at 300 K. We succeeded in the rapid fabrication of perpendicularly connected molecular lines of adsorbed ALM and styrene (and 2,4-dimethylstyrene) through radical-initiated chain reaction along and across the dimer rows on the Si(100)−(2 × 1)−H surface. The continuous growth of styrene lines at the end DB of a growing ALM line (or vice versa) was not achieved, perhaps due to steric hindrance or/and interaction between intermediate radical of styrene and adsorbed ALM. By exploring the optimum conditions for the chain reaction of different molecules, the present methods for the fabrication of interconnected molecular lines have the potential to be used in predesigned nanoscale wiring and formation of molecular junctions on the Si(100)−(2 × 1)−H surface.

Supporting Information Available: STM images showing the growth of ALM line to connect a preexisting styrene line (Figure S1) and interconnection of ALM and 2,4-DMS lines (Figure S2). This material is available free of charge via Internet at http://pubs.acs.org.

References and Notes

(1) (a) Aviram, A.; Ratner, M. A. *Chem. Phys. Lett.* **1974**, *29*, 277. (b) Joachim, C.; Gimzewski, J. K.; Aviram, A. *Nature (London)* **2000**, *408*, 541.

(2) Nitzan, A.; Ratner, M. A. *Nature (London)* **2003**, *300*, 1384.

(3) (a) Ratner, M. *Nature (London)* **2005**, *435*, 575. (b) Guisinger, N. P.; Yoder, N. L.; Hersam, M. C. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 8838.

(4) (a) Wolkow, R. A. *Annu. Rev. Phys. Chem.* **1999**, *50*, 413. (b) Bent, S. F. *Surf. Sci.* **2002**, *500*, 879. (c) Hamers, R. J. *Nature (London)* **2001**, *412*, 489.

(5) Nogami, J. *Surf. Rev. Lett.* **2000**, *7*, 555 and references therein.

(6) Gambardella, P.; Blanc, M.; Brune, H.; Kuhnke, K.; Kern, K. *Phys. Rev. B* **2000**, *61*, 2254.

(7) Lopinski, G. P.; Wayner, D. D. M.; Wolkow, R. A. *Nature (London)* **2000**, *406*, 48.

(8) Piva, P. G.; DiLabio, G. A.; Pitters, J. L.; Zikovsky, J.; Rezeq, M.; Dogel, S.; Hofer, W. A.; Wolkow, R. A. *Nature (London)* **2005**, *435*, 658.

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

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

(11) Cho, J. H.; Oh, D. H.; Kleinman, L. *Phys. Rev. B* **2002**, *65*, 081310.

(12) DiLabio, G. A.; Piva, P. G.; Kruse, P.; Wolkow, R. A. *J. Am. Chem. Soc.* **2004**, *126*, 16048.

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

(14) Linford, M. R.; Fenter, P.; Eisenberger, P. M.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1995**, *117*, 3145.

(15) Kang, J. K.; Musgrave, C. B. *J. Chem. Phys.* **2002**, *116*, 9907.

(16) Schäfer, K.; Bonifačić, M.; Bahnemann, D.; Asmus, K.-D. *J. Phys. Chem.* **1978**, *82*, 2777.

(17) Zhang, X.; Zhang, N.; Schuchmann, H. P.; Sonntag, C. V. *J. Phys. Chem.* **1994**, *98*, 6541.

(18) Boland, J. J. *J. Vac. Sci. Technol., A* **1992**, *10*, 2458.

(19) Shen, T. C.; Wang, C.; Abeln, G. C.; Tucker, J. R.; Lyding, J. W.; Avouris, Ph.; Walkup, R. E. *Science* **1995**, *268*, 1590.