

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/215559898>

Chemical Modification and Patterning of Iodine-Terminated Silicon Surfaces Using Visible Light

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY B · MARCH 2002

Impact Factor: 3.3 · DOI: 10.1021/jp013523h

CITATIONS

63

READS

35

5 AUTHORS, INCLUDING:



Wei xing Cai

Chinese Academy of Sciences

27 PUBLICATIONS 1,842 CITATIONS

SEE PROFILE



Robert J. Hamers

University of Wisconsin-Madison

386 PUBLICATIONS 17,300 CITATIONS

SEE PROFILE

Chemical Modification and Patterning of Iodine-Terminated Silicon Surfaces Using Visible Light

Wei Cai, Zhang Lin, Todd Strother, Lloyd M. Smith, and Robert J. Hamers*

Department of Chemistry, University of Wisconsin—Madison, 1101 University Avenue,
Madison, Wisconsin 53706-1396

Received: September 13, 2001; In Final Form: December 4, 2001

The use of iodine as a photolabile passivating agent for photochemical modification of silicon surfaces is demonstrated. X-ray photoelectron spectroscopy measurements show that iodine termination using iodine dissolved in benzene leads to Si surfaces exhibiting higher iodine surface coverages and lower levels of carbon contamination than previous methods. When exposed to 514 nm light in the presence of a suitable reactive molecule, such as an organic alkene, the surface iodine is removed and the reactive molecule links to the silicon surface. The results of experiments in which the polarization and angle of the incident light were varied show that the reaction mechanism is mediated by absorption of light in the bulk Si. A much greater photoattachment efficiency is obtained on heavily doped n-type silicon than on p-type silicon. It is proposed that on n-type silicon samples the photogenerated minority carriers (holes) accumulate near the surface, making the surface more susceptible to nucleophilic attack by the alkene molecules. The use of this method for photopatterning a Si surface with specific reactive groups is demonstrated.

Introduction

The preparation and patterning of organic monolayers on surfaces is currently an area of intense interest, because of the use of organic molecules as active elements in microelectronics^{20,26} and the development of new molecular⁷ and bimolecular^{15,23} electronic devices. To integrate these new organic-based materials with existing silicon-based microelectronics technologies, improved strategies for chemical functionalization and patterning of silicon surfaces must be developed.^{3,14} Previous studies have shown that silicon surfaces on which the exposed surface atoms are passivated with a layer of hydrogen atoms (hydrogen-terminated silicon surfaces) can serve as a starting point for further modification, via reaction with functionalized alkenes.^{3,9,18,29–31,35} Since hydrogen-passivated Si surfaces are quite unreactive toward alkene molecules, these reactions must generally be activated, through the use of radical initiators,^{17,18} heat,^{18,27} or light.^{5,9,29,30}

The use of light to activate surface chemical modification is particularly attractive, because it provides a means for direct photopatterning of specific functional groups on surfaces. For example, hydrogen-terminated Si surfaces can be reacted with ω -functionalized 1-alkenes by initiating the surface reactions with ultraviolet light.^{9,29,30} This method can be used to produce Si surfaces terminated with specific functional groups such as amines and carboxylic acid groups; these modified surfaces can in turn be used to attach more complex molecules such as DNA to silicon surfaces.^{29,30}

One drawback to the use of H-terminated silicon, however, is that previous studies using simple alkenes and alkynes have shown that attachment of these molecules on H-terminated silicon only occurs when the excitation wavelength is <350 nm.⁵ Since many molecules absorb in the ultraviolet (UV)

region, the use of UV excitation has the possibility of inducing side reactions such as polymerization reactions.⁴

Recent studies have shown that Si surfaces can also be terminated with iodine atoms.^{11,13,16,24} Iodosilane compounds are known to undergo photochemical reactions analogous to those of organic iodines,⁸ suggesting that I-terminated Si surfaces may provide a potentially attractive alternative to H-terminated Si for photochemical patterning and modification. In this paper, we report a new method for preparing I-terminated Si surfaces, and we show that these I-terminated surfaces can be chemically patterned with specific functional groups using visible light. The variation in reaction efficiency as a function of the polarization of the light, the angle of incidence, and the bulk doping of the substrates provides insights into the mechanism of the photochemical reaction.

Experimental Section

All chemicals were reagent grade or better and used as received unless otherwise specified. Solutions were made with deionized water (18 M Ω ·cm resistivity). Other reagents include methanol (Fisher), hydrochloric acid (EM Science), ammonium fluoride (40%, Merck), Si(001) wafers (Virginia Semiconductor), Si(111) wafers (Semiconductor Processing Corp.). The 2,2,2-trifluoroethyl ester of 10-undecylenic acid (TFEU) was synthesized as described previously.²⁹ All other chemicals were obtained from Aldrich.

Experiments were conducted using both (111)- and (001)-oriented silicon substrates. These surfaces were first terminated with H atoms following well-established procedures, and the H atoms were then replaced with I atoms to produce I-terminated Si surfaces.^{13,16,28} Because previous studies have shown that the optimal procedure for H-termination is different for the (111) and (001) crystal faces,¹⁰ a slightly different procedure was followed for (111) and (001) orientations. Si(111) samples were first ultrasonically cleaned in acetone followed by methanol (5

* Corresponding author: Phone: 608-262-6371. Fax: 608-262-0453.
E-mail: rjhamers@facstaff.wisc.edu.

min each) and then oxidized by a 1:1:5 hydrogen peroxide–ammonium hydroxide–water solution and by a 1:1:5 hydrogen peroxide–hydrochloric acid–water for 10 min each at 80 °C. The oxidized samples were then immersed in a solution of NH_4F solution (40 wt %) for 5 min and then rinsed for about 1 min with ultrapure deionized water. Si(001) samples were prepared by cleaning in acetone followed by methanol and then oxidized by a hydrogen peroxide–ammonium hydroxide–water solution (1:1:4) for 5 min at 75 °C. After 1 min etching in 1% aqueous HF solution to H-terminate the silicon atoms, the samples were rinsed with deionized water and blown dry under a stream of nitrogen gas.

Because our procedures for I-termination and subsequent photochemical modification are different from those used previously, these procedures are presented in the “Results” section below. The photoreactions were initiated using the 514 nm line from a 100-mW air-cooled Omnicrome argon ion laser. In some experiments, the 514 nm line (1 W) from a Spectra-Physics argon ion laser system was used. In all experiments, the beam was typically expanded to a diameter of approximately 1.5 cm, providing intensities of $\sim 50\text{--}500\text{ mW/cm}^2$.

X-ray photoelectron spectroscopy (XPS) was used to characterize the I-termination and the subsequent photochemical modification of the surfaces. XPS data were obtained using a Physical Electronics system with monochromatized Al $K\alpha$ radiation (1486.6 eV). The samples were oriented so that the detector collected photoelectrons ejected at an angle of 40° from the surface normal. The Si(2p) peaks were measured and used as an internal standard for both energy and intensity. Apparent shifts in binding energy can arise from chemical shifts (i.e., changes in binding energy due to local changes in chemical environment) as well as changes in the bulk Fermi energy with respect to the energy bands (due, for example, to changes in bulk doping). Unless stated otherwise, the spectra reported here are the *corrected* binding energies, obtained by applying a rigid shift to all binding energies of each sample to bring the binding energy of the bulk Si(2p_{3/2}) peak to a fixed value of 99.4 eV. Differences in the uncorrected Si(2p) binding energies reflect changes in the bulk Fermi energy of different samples, while shifts in the corrected binding energies reflect true changes in local chemical environment. The integrated intensity of the bulk Si signal was used as an internal standard for quantitative analysis. XP spectra were analyzed using standard curve fitting procedures, in which the quality of fit was evaluated through a “quality-of-fit” parameter based on a reduced χ^2 .² In general, a smaller reduced χ^2 represents a better fit, with values of equal or less than 1 indicating that the fit and the data are indistinguishable within the experimental noise.

Results

(a) Iodine Termination. Previous studies have prepared I-terminated Si samples by immersing the H-terminated surfaces into solutions of iodine dissolved in ethanol or methanol.^{11,13,16,28} However, it was also reported that the resulting surfaces have strongly adsorbed alkoxy groups, with only ~ 0.25 monolayer of iodine.^{11,16} We therefore examined iodine termination in less reactive solvents. Previous studies under ultrahigh vacuum conditions have shown that benzene will bond to silicon surfaces; however, desorption occurs at a relatively low temperature of 350 K with no fragmentation.^{12,19} This reversible behavior, together with the high solubility of iodine in benzene, suggested the possibility of using benzene as an alternative solvent for iodine termination of Si.

Figure 1 compares the I(3d) and C(1s) spectra of two I-terminated Si(111) samples that were prepared identically,

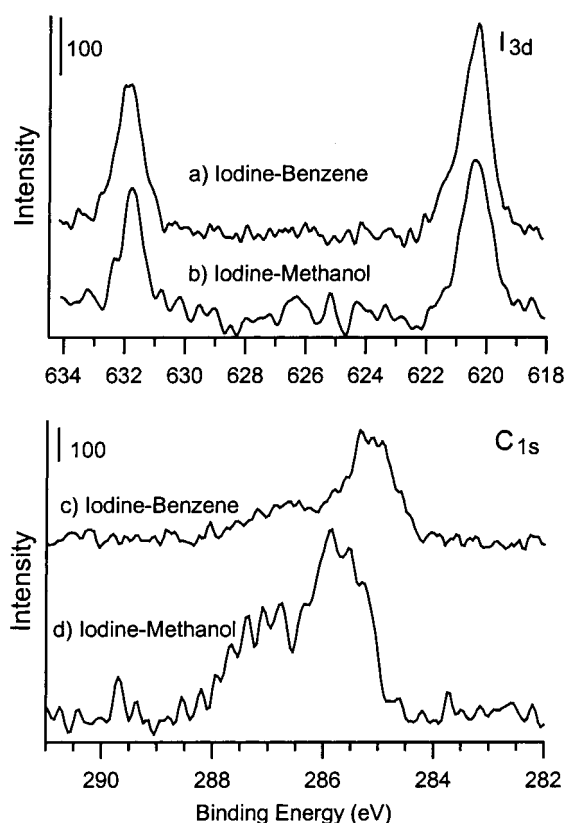


Figure 1. Iodine(3d) and carbon(1s) XP spectra of Si(111) sample reacted with saturated solutions of iodine/benzene and iodine/methanol, for 20 min: (a) I(3d), immersed in iodine/benzene; (b) I(3d), immersed in iodine/methanol; (c) C(1s), immersed in iodine/benzene; and (d) C(1s), immersed in iodine/methanol.

except for the solvent used during the iodine termination step. Parts a and c of Figure 1 show the I(3d) and C(1s) spectra of a H-terminated Si(111) sample that was immersed in a saturated solution of I_2 /benzene for 20 min. Spin–orbit splitting in iodine leads to distinguishable 3d_{5/2} and 3d_{3/2} components from the 3d core level, with a 6:4 intensity ratio. This sample yields strong iodine peaks at 620.3 eV (3d_{5/2}) and 631.8 eV (3d_{3/2}) with a full-width at half-maximum (fwhm) of 1.0 eV, close to the resolution of the XPS system. The narrow width and symmetric shape indicate there is only one type of iodine adsorbed on the surface. The C(1s) spectrum (Figure 1c) shows a small amount of carbon with a binding energy of 285.1 eV and a shoulder at 286.7 eV. For comparison, Parts b and d of Figure 1 show the I(3d) and C(1s) spectra of a H-terminated Si(111) sample after immersion in a saturated solution of I_2 in methanol for 20 min. The I(3d) lines from the I_2 /methanol sample are again relatively narrow, but they are less intense than those from the I_2 /benzene sample. The C(1s) spectrum of the I_2 /methanol sample (Figure 1d) shows two peaks at binding energies of ~ 285.7 and 287.1 eV. The C(1s) spectra of the two samples show differences in binding energies that reflect differences in the type of residual organic matter on the surface. The more important comparison, however, is that a quantitative analysis of the peak areas (normalized to the area of the bulk Si(2p), as an internal standard) shows that the samples prepared by immersion in I_2 /benzene yield an I(3d)/Si(2p) area ratio that is 1.8 times that of samples prepared by immersion in I_2 /methanol and a corresponding C(1s)/Si(2p) ratio only 0.5 times as large. Thus, the XPS data show that iodine-passivated Si(111) surfaces have higher levels of iodine coverage and lower levels of carbon contamination when formed in I_2 /benzene than in I_2 /methanol.

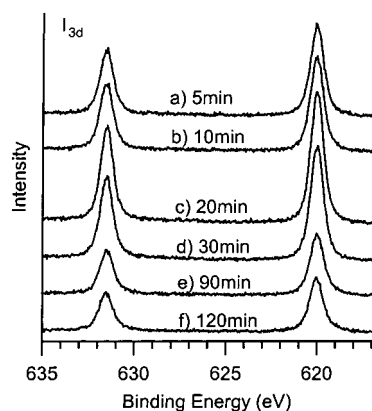


Figure 2. Iodine(3d) XP spectra of Si(111) reacted with iodine/benzene solution for different time periods: 5 min, 10 min, 20 min, 30 min, 90 min, and 120 min.

To determine the absolute I coverage, the I(3d)/Si(2p) area ratio was compared to that obtained from a Si(001) sample that was prepared in ultrahigh vacuum and then immediately exposed to a saturation coverage of methyl iodide (CH_3I). Previous measurements have shown that CH_3I adsorbs dissociatively to yield Si-CH₃ and Si-I species with a density of $(2.9 \pm 0.3) \times 10^{14} \text{ cm}^{-2}$.⁶ We find that the I/Si ratio produced by immersing H-terminated Si(111) in I_2 /benzene as described above is 0.76 times that of the sample prepared in UHV and then exposed to CH_3I , thereby implying that the density of I atoms at the surface is $2.2 \times 10^{14} \text{ cm}^{-2}$. Since the bulk-truncated Si(111) surface has $6.8 \times 10^{14} \text{ atoms/cm}^2$, we conclude that the samples exposed to I_2 /benzene have only approximately one iodine atom per three surface silicon atoms, and presumably, the remaining Si atoms remain terminated with hydrogen. The I coverage for samples immersed in I_2 /methanol is only ~ 0.18 monolayer; this number is comparable to, but slightly smaller than, that obtained in a previous measurement.¹¹ Thus, the "I-terminated" samples are in fact only incompletely terminated with I atoms.

While the data in Figure 1 were obtained using a fixed immersion time of 20 min for replacement of the surface H atoms with I atoms, experiments were performed to identify the optimal duration of immersion to achieve the best iodine termination. Figure 2 shows the XP spectra of H-terminated wafers that were immersed into a saturated solution of iodine dissolved in benzene for various periods of time. The I(3d_{5/2}) and I(3d_{3/2}) peak intensities increase as the reaction time increases from 5 to 20 min. However, immersion times longer than 20 min yield almost no further increase in the I coverage. After long periods of time the O(1s) spectrum (not shown) shows evidence for surface oxidation, likely due to either minute traces of water in the benzene or to incomplete removal of dissolved oxygen in the solvent.

Although the data shown here was obtained on the Si(111) surface, similar experiments on (001)-oriented Si samples yielded comparable results. On both (111) and (001) surfaces, immersion of H-terminated samples in I_2 /benzene for 20 min yields surfaces with only low levels of contamination. However, our data indicates that I-termination using I_2 /benzene or I_2 /methanol yields surfaces at which only *some* of the surface H atoms are replaced with iodine, so that the "I-terminated" surfaces are actually a mixture of Si-I and Si-H species. Because samples produced via immersion in I_2 /benzene show lower levels of contamination by carbon and oxygen and show significantly more iodine at the surface than samples produced by immersion in I_2 /methanol, we used the I_2 /benzene method for all subsequent studies.

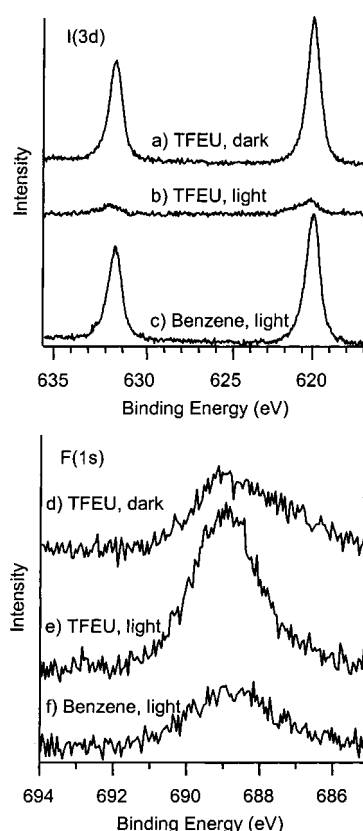


Figure 3. Iodine (3d) and fluorine(1s) XP spectra of Si(111)/I surfaces exposed to 514 nm light for 4 h and the dark control: (a) I(3d), covered with 2,2,2-trifluoroethyl ester of 10-undecylenic acid (TFEU) and kept in the dark; (b) I(3d), TFEU, illuminated; (c) I(3d), benzene, illuminated; (d) F(1s), TFEU, dark; (e) F(1s), TFEU, illuminated; and (f) F(1s), benzene, illuminated.

(b) Photochemical Modification of I-Terminated Samples.

The procedure for photochemical modification of I-terminated Si samples is similar to that we used previously for photochemical modification of H-terminated samples,^{29,30} except that for the I-terminated samples light of longer wavelength (514-nm) was used. Each sample of I-terminated Si was placed in a Teflon cell equipped with a quartz window and a nitrogen purge. A thin layer of the molecule of interest was formed by depositing a $\sim 10 \mu\text{L}$ aliquot onto the I-terminated Si sample; the liquid typically spread via nascent wetting over a region $\sim 1 \text{ cm} \times 1 \text{ cm}$ in size. The cell containing the sample was then sealed and purged continuously with a small flow of dry nitrogen and illuminated with 514 nm light from an argon ion laser (typically $\sim 50\text{--}500 \text{ mW/cm}^2$ for 3–4 h). After photoreaction, each sample was immersed in chloroform and then in methanol ($\sim 10 \text{ min}$ each) in an ultrasonic bath to help remove any physisorbed species.

Figure 3 shows the I(3d) spectra (Figure 3a–c) and the F(1s) spectra (Figure 3d–f) of iodine-terminated Si(111) surfaces prepared as above, along with two different control samples. Figure 3a shows the I(3d) spectrum of a "dark" control surface, consisting of a sample that was I-terminated and covered with a layer of TFEU for 4 h, but was not exposed to light. This sample yields a large I(3d) signal, and analysis of the peak area shows that the I(3d) area is nearly identical to that observed on freshly I-terminated samples. Figure 3b shows the I(3d) spectrum of an identical sample that was I-terminated, covered with TFEU, and was then illuminated with 514 nm light (0.5 W/cm^2) for 4 h. This sample shows a much smaller I(3d) intensity, only

10% of that observed on the dark control sample. Thus, it appears that the illumination leads to the loss of iodine from the surface.

To determine whether iodine could desorb from the I-terminated surface into a simple solvent, a second control experiment was performed in which an I-terminated Si(111) sample was covered by benzene and then illuminated in the same manner as above (0.5 W/cm^2 for 4 h). The I(3d) spectrum of this sample (Figure 3c) shows almost the same I(3d) intensity as the dark control (Figure 3a). Thus, even though benzene is a good solvent for iodine, illumination of the sample covered with a layer of benzene leads to no significant loss of iodine.

While the I(3d) spectra provide information on the loss of iodine, the F(1s) spectra provide information on the attachment of organic molecules to the same samples. The sample that was exposed to TFEU and illuminated (Figure 3e) yields one strong peak at 689.0 eV, which we attribute to the fluorine atoms in the trifluoroethyl ester group of TFEU. However, both control samples (Figure 3d,f) also show some fluorine at a slightly lower binding energy of 688.7 eV. Since the benzene control sample was exposed to F only during the initial $\text{NH}_4\text{F}/\text{HF}$ etch, the F peak from that sample (Figure 3f) must arise from F atoms left on the surface from the H-termination step. Indeed, previous studies of silicon wet etching in $\text{NH}_4\text{F}/\text{HF}$ have shown that this process leaves behind a small quantity (~ 0.25 monolayer) of F atoms bonded to the Si surface.²⁵ Since Si has a smaller electronegativity (Pauling electronegativity = 1.90) than C (Pauling electronegativity = 2.55) does, the F(1s) binding energies of F atoms bonded directly to the Si surface are expected to be slightly smaller than those that are part of the CF_3 group in the TFEU molecule, in agreement with the 0.3 eV decrease in binding energy we observed when comparing the F signals in Figure 3f (688.7 eV) to those from the TFEU molecule (689.0) in Figure 3e. The origin of the small, asymmetric F signal in the TFEU "dark" control sample (Figure 3d) likely arises from a mixture of residual F from the $\text{NH}_4\text{F}/\text{HF}$ termination step and some small attachment (physisorbed or covalently linked) of the TFEU molecule. Nevertheless, the very significant increase in intensity of the F(1s) peak when exposed to TFEU and illuminated shows that the illumination with 514 nm light induces attachment of the TFEU molecule to the surface.

The absence of reaction with benzene, even when illuminated, suggests that the iodine removal and molecular attachment may require the presence of a reactive group in the liquid-phase molecule. To identify whether the reactivity of TFEU is directly associated with the vinyl group, another set of experiments was performed to compare the reaction efficiencies of two molecules that have very similar structures but differ in whether there is an alkene group. The molecules chosen for this comparison are 1*H*,1*H*,2*H*-perfluoro-1-dodecene (PFD) and perfluorononane. Figure 4a shows the I(3d) spectrum of an I-terminated sample that was covered with PFD, while Figure 4b shows the I(3d) spectrum of an identical sample that was illuminated ($\sim 0.5 \text{ W/cm}^2$, 4 h). Comparing the PFD sample that was illuminated (Figure 4b) with the sample left in the dark (Figure 4a) shows that illumination in the presence of this alkene results in nearly complete disappearance of the iodine signal. Figure 4c shows the I(3d) spectrum from an I-terminated surface that was covered with perfluorononane and then illuminated. In contrast to the results from the PFD, the sample covered with perfluorononane and illuminated exhibits a high I(3d) signal. Thus, the XPS data show that the vinyl group (or some other suitable reactive group) is necessary in order for I to be removed from the surface.

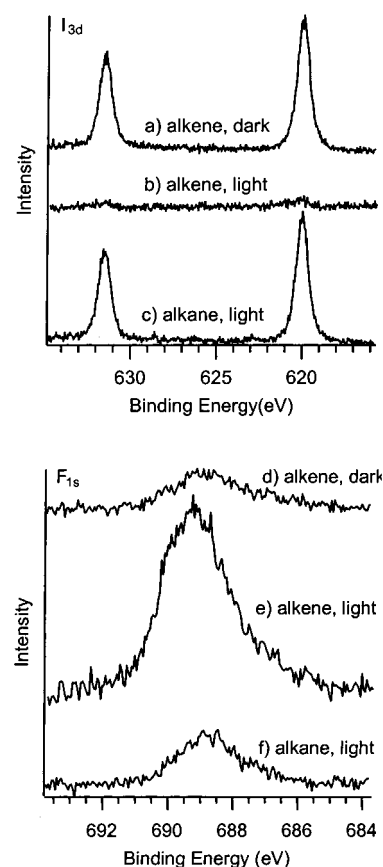


Figure 4. Iodine (3d) and fluorine (1s) XP spectra of I-terminated Si(111) surfaces exposed to PFD or perfluorononane and exposed to 514 nm light for 4 h and the controls: (a) I(3d), PFD, dark; (b) I(3d), PFD, illuminated; (c) I(3d), perfluorononane, illuminated; (d) F(1s), PFD, dark; (e) F(1s), PFD, illuminated; and (f) F(1s), perfluorononane, illuminated.

The changes in I(3d) intensity are accompanied by changes in the F(1s) intensity. Some F(1s) intensity is observed even on the control sample left in the dark (Figure 4d); we again attribute this F signal to a combination of persistently bound F atoms from the $\text{NH}_4\text{F}/\text{HF}$ treatment²⁵ and a small quantity of physisorbed or chemisorbed PFD molecules. The F(1s) signal of the sample exposed to light and the 1*H*,1*H*-2*H*-perfluoro-1-dodecene (Figure 4e) shows by far the largest F(1s) peak, with an area ratio $A_{\text{F}(1s)}/A_{\text{Si}(2p)}$ 3.4 times that of the sample left in the dark. As expected, the saturated alkane, perfluorononane, shows the smallest F(1s) signal, which is not significantly different from that of the dark control. Thus, the XPS data show that photoattachment and the loss of iodine both require light and a suitable reactant molecule, such as an alkene.

(c) Chemical Photopatterning. To demonstrate the use of this reaction to photopattern specific chemical groups on a surface, we performed experiments in which a hydrophilic molecule (TFEU, subsequently hydrolyzed to the free acid form) and a hydrophobic molecule (dodecene) were selectively bonded to specific regions of the sample. In this experiment, an iodine-terminated surface with an area of 1.5 cm^2 was put in the reaction cell and covered with a thin layer of TFEU. A stainless steel mask with two circular openings of 2.3 mm diameter, 5.4 mm apart, was placed on top of the sample and ester layer and was held in place by surface tension. The reaction cell was covered with a quartz window and illuminated with 514 nm laser light (40 mW/cm^2 , directed perpendicular to the surface) for 3 h under dry nitrogen. The mask was then removed and the sample was rinsed with dodecene. In a second stage, the

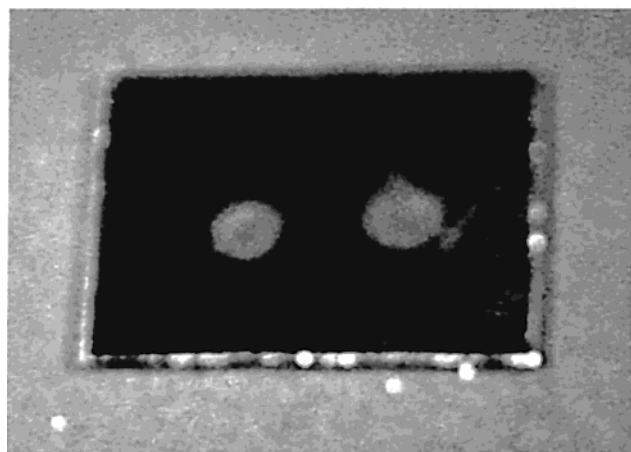


Figure 5. Si(001) sample that was prepared as described in text and then photographed using oblique illumination. Water condensation in the central spots, where acid-terminated, leads to increased scatter and makes them appear light. The remaining surface areas were functionalized with dodecene; these areas do not condense water vapor and therefore appear dark.

sample was returned to the cell, and the entire sample was covered with a thin layer of dodecene and irradiated for another 2 h, to attach dodecene to the remainder of the sample. At this stage the modified surface was expected to have the trifluoro ester termination in the two spots and alkane termination from dodecene in the surrounding periphery. To hydrolyze the ester-terminated regions to the free acid form, the entire sample was then immersed in a 250 mM solution of potassium *tert*-butoxide in dimethyl sulfoxide for 3 min at room temperature, followed by rinsing in HCl solution (pH 2.0), in accordance with a previously developed procedure for forming acid-terminated Si surfaces.²⁹

The resulting spatial variations in chemical composition led to very different wetting properties that can be observed by direct visual inspection. After the sample is cooled to 0 °C, when it is returned to ambient conditions, moisture in the air condenses readily in the central acid-terminated regions, while little or no condensation occurs in the outer areas, where the more hydrophobic dodecene molecules were attached. Figure 5 shows a photograph of a sample prepared as described above and then illuminated at an oblique angle. The central spots are bright because water condensation in the hydrophilic central two spots leads to increased scattering of obliquely incident light. When the sample is dry, however (not shown), there is no detectable difference between them.

(d) Mechanism of Iodine Removal and Molecular Attachment. Because previous experiments on H-terminated silicon have shown that bonding of alkenes can be induced thermally,^{18,27} we conducted a set of experiments to test for any thermal effects arising from illumination of the I-terminated Si. To measure the temperature rise, a very small thermocouple junction was attached directly to the front face of the sample with a clear adhesive, and the temperature was measured during illumination. At 1 W total power (~ 0.5 W/cm²), a temperature rise of ~ 15 °C was observed. To determine whether this temperature rise might induce a thermal reaction, a control experiment was performed in which an I-terminated sample was covered with TFEU and heated to 47 °C for 2 h under dark conditions, and a second identical sample was covered with TFEU and maintained in the dark at room temperature (26 °C). Analysis via XPS of the sample that was heated yielded an I/Si area ratio of 1.3, a F/Si ratio of 0.18, and a C/Si ratio of 0.59. For comparison, the sample that was maintained at room

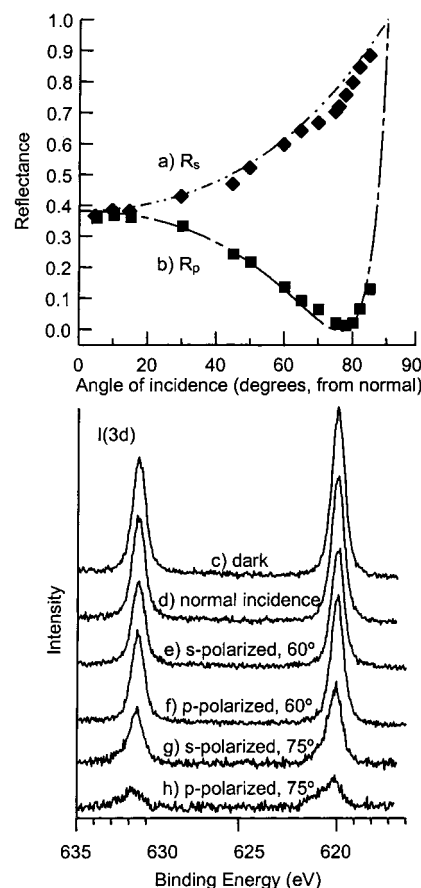


Figure 6. (a) Measured reflectance of I-terminated n-type ($0.005 \Omega \cdot \text{cm}$) Si(111) sample as a function of incidence angle, using s-polarized light. Experimental points are shown as diamonds. Calculated values using optical constants for pure (undoped) Si are shown as a dashed line. (b) Reflectance of I-terminated n-type Si(111) sample using p-polarized light. Experimental points are shown as squares. Calculated values using optical constants for pure (undoped) Si are shown as a dashed line. (c–h) I(3d) XP spectrum of I-terminated Si(111) surfaces that were covered with TFEU and exposed to p- and s-polarized light at different incident angles: (c) dark control (not exposed to light); (d) exposed to light at an incidence angle of 0° (from surface normal); (e) exposed to s-polarized light, incidence angle = 60°; (f) exposed to p-polarized light, incidence angle = 60°; (g) exposed to s-polarized light, incidence angle = 75°; and (h) exposed to p-polarized light, incidence angle = 75°.

temperature yielded an I/Si area ratio of 1.3, a F/Si ratio of 0.19, and a C/Si ratio of 0.78. These values are close to each other and close to those of the other “dark” control experiments. The absence of any decrease in the I/Si ratio or any increase in the F/Si or C/Si ratios for the warmed sample demonstrates that although there is a small temperature rise, it does not induce any significant loss of iodine or attachment of TFEU to the sample.

Experiments were also conducted to identify whether the angle of incidence and the polarization of the light affect the reaction efficiency. The traces in parts a and b of Figure 6 show the measured values of reflectance from a clean, I-terminated surface as a function of incidence for s- and p-polarized 514 nm light, respectively. Also shown (dash lines) are the values of reflectivity calculated using the Fresnel equations and the bulk optical constants for pure (undoped) Si. The good agreement between the experimental values measured on the doped Si samples and the calculated values using the values for undoped Si show that the optical properties of Si do not depend on the doping of the sample.

Figure 6c–h shows the residual I(3d) signals from samples that were covered with TFEU and illuminated with s- and p-polarized light at various angles of incidence, along with a control sample left in the dark. Measurements of photoattachment efficiency at different angles of incidence are difficult to compare quantitatively because of the cell geometry used and the need to maintain the sample in a horizontal position. However, at any fixed angle, comparison of s- and p-polarized light can be achieved using a polarizer and a $\frac{1}{4}$ -wave plate (which rotates the polarization vector of the light). At normal incidence, the I signal is almost the same as that of the dark control. In other experiments, however, we have observed that illumination at normal incidence does induce loss of iodine and subsequent molecular attachment, but at a comparatively slow rate. While the data in Figure 6 show only one “dark” control, quantitative analysis and normalization of the individual sets of measurements summarized there show that at high angles of incidence s-polarized light produces no significant loss of iodine, while p-polarized light does. The loss of iodine is significantly more effective at an incidence angle of 75° than closer to the surface normal and is most effective with p-polarized light.

The reflectivity data in Figure 6a,b show that at 75° incidence angle, the reflectivity from clean silicon for p-polarized light reaches a minimum, while the s-polarized light still has a reflectance of ~ 0.7 . Thus, the amount of light absorbed by the sample ($1 - R$) is approximately 3 times higher when using p-polarized light than when using s-polarized light. Although the optical boundary conditions will be perturbed somewhat by the thin liquid film of reactant molecules (not included in Figure 6a,b), the effectiveness of iodine removal roughly corresponds with the fraction of light absorbed by the sample. Corresponding measurements of the molecular F(1s) signals (not shown) reveal that the samples with greatest loss of iodine also show the greatest degree of molecular attachment.

The angle- and polarization-dependent measurements indicate that the reaction probability is highest when the amount of light absorbed by the silicon sample is highest. This suggests that the photoattachment may involve photoexcited electrons and holes in the bulk. Since the behavior of electron–hole pairs depends strongly on the bulk doping of the material, we compared the reaction efficiency on samples with different bulk doping. Experiments were performed on highly doped n-type ($0.005 \Omega \text{ cm}$, As-doped), lightly doped n-type ($10 \Omega \text{ cm}$, P-doped), heavily doped p-type ($0.1 \Omega \text{ cm}$, B-doped), and lightly doped p-type ($20 \Omega \text{ cm}$, B-doped) samples. For each doping, we first passivated the surfaces with iodine as described above, and measured the I(3d) and Si(2p) XPS intensities. The I(3d)/Si(2p) ratio was identical on all the samples, indicating that formation of the iodine-passivated surface does not depend on the bulk doping. A strong doping dependence is observed, however, in the photoattachment step. Figure 7 shows the I(3d) and F(1s) spectra of the iodine-terminated Si(111) samples of different bulk dopings that were exposed to TFEU and irradiated with 514 nm light (0.5 W/cm^2) for 5 h. The XPS spectra show that the residual iodine signal from the n-type, heavily doped sample ($0.005 \Omega \text{ cm}$ resistivity) is only 0.2 times that of the lightly doped n-type sample ($10 \Omega \text{ cm}$) and only ~ 0.14 times those of p-type samples. Thus, iodine is most effectively removed from the highly doped n-type sample. The F(1s) signal intensity shows that the decrease in iodine signal is accompanied by a corresponding increase in the F(1s) signal from the adsorbed molecules. As expected, the highly doped n-type sample shows the highest F signal, while the p-type samples

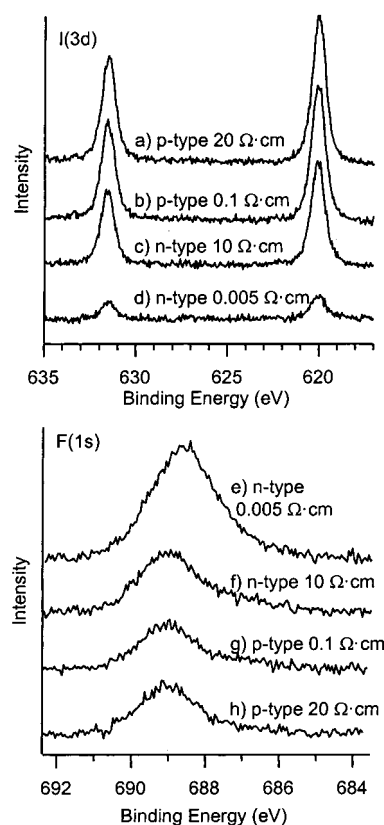


Figure 7. XPS spectra of different Si(111) substrates exposed to TFEU and p-light for 5 h, as described in text.

show the lowest. Thus, the removal of iodine and the attachment of the alkene are most efficient on heavily doped n-type samples.

To investigate how the bulk doping of the silicon affected the near-surface electronic structure, we performed measurements of the surface photovoltaic effect. In these experiments, I-terminated Si samples were covered with benzene, and a platinum electrode was placed $\sim 0.5 \text{ mm}$ away, in contact with the liquid but not in direct contact with the sample. The sample was then illuminated with light (514 nm , $\sim 45 \text{ mW/cm}^2$) that was modulated with a mechanical chopper, and the photoinduced changes in surface potential were measured by coupling the Pt electrode to a lock-in amplifier. Measurements on n-type and p-type samples both showed a photovoltaic effect of comparable magnitude, but with a reversal of sign (180° phase shift) between n-type and p-type samples. While it is possible in principle to quantitatively measure the surface photovoltaic effect using this method, in practice the intensities that would be needed are prohibitively high, and the observed photovoltage can only be taken as a qualitative indication of the extent of near-surface band-bending. Since a photovoltaic effect is only observed when the semiconductor bands are bent, this result indicates that the I-terminated, n-type Si samples have an upward band-bending and the I-terminated, p-type Si samples have a downward band-bending. Thus, the Fermi level is apparently pinned somewhere in the middle of the band gap, but not near either edge.

Discussion

Our results show that it is possible to chemically pattern silicon surfaces using visible light of moderate intensity, by starting with iodine-terminated silicon. While there are many possible routes to prepare iodine-terminated Si surfaces, the XPS data in Figure 1 show that using benzene as the solvent leads to iodine-terminated surfaces exhibiting a higher iodine coverage

and a lower degree of carbon contamination than the previously used scheme, in which methanol or ethanol was used as a solvent.

The lower degree of carbon contamination using benzene as a solvent during the iodination step is consistent with a previous study of organo-silicon iodide compounds (i.e., compounds of the form R_3Si-I),⁸ which showed that upon illumination with short-wavelength radiation, these undergo photochemical reaction with solvents such as methanol and ethanol. While the reactivity of small silanes may be different from that of an extended Si surface, this earlier study proposed that optical excitation produced cationic Si^+ species that were susceptible to nucleophilic attack by the solvent, producing species of the form $R_3Si-OCH_3$. Similarly, recent studies of I-terminated Si samples produced by immersion in methanol have observed persistently bound alkoxy groups after immersion of H-terminated Si surfaces into I_2 /methanol.²⁴ In contrast, our XPS data show that there is essentially no reaction with benzene, even in the presence of optical excitation. Consequently, using benzene as a solvent during I-termination leads to less carbon contamination and yields higher I coverages. However, it is important to note that even with benzene, the iodine coverage is still much smaller than the total number of surface Si atoms. Further studies will be needed to more clearly elucidate the chemical and structural composition of the surfaces.

In the subsequent photochemical attachment of molecules, the intensity of the I(3d) signal provides quantitative information on the extent of iodine removal, while the F(1s) signal reveals the extent of molecular attachment. From our studies, there are three key pieces of information that provide insight into the mechanism of the photochemical attachment. The first is that the XPS data show that iodine is *not* removed, even upon illumination, when the sample is in contact with a nonreactive molecule such as a simple alkane (Figure 4c,f) or benzene (Figure 3c,f). The second is that the photochemical attachment is much more facile on n-type silicon than on p-type silicon. The third is that the angle- and polarization-dependent data show that reaction can be initiated by light incident at all angles of incidence, but is most efficient with p-polarized light at moderately high angles of incidence ($\sim 70^\circ$).

Since iodine is not removed and no significant molecular attachment is observed when I-terminated Si is immersed in benzene or simple alkanes, it is clear that removal of iodine and molecular attachment are not independent. These results suggest that the photochemical attachment of organic molecules on I-terminated surfaces involve a *concerted* process in which optically induced changes in the surface facilitate reaction with molecules in the thin film.

The XPS data show that iodine removal and molecular attachment are both much more facile on n-type silicon than p-type silicon. Reflectivity measurements such as those in Figure 6 show that the optical constants of Si are nearly independent of doping at the levels used here, so that the doping dependence cannot be attributed to differences in reflectivity at the liquid–solid interface. Thus, the dependence on doping shows that the reaction must involve absorption of the light by the bulk Si. Since previous studies of H-terminated Si have shown that H atoms can be removed via direct excitation of a $\sigma-\sigma^*$ transition (involving energies of $\sim 6-8$ eV),^{1,33,34} we also considered the possibility of direct photochemical excitation of a Si–I bond as a possible mechanism. However, while on the Si(111) surface the Si–I bond is oriented perpendicular to the surface, we find that the iodine removal and molecular attachment occur when the electric field vector of the light is parallel to the surface

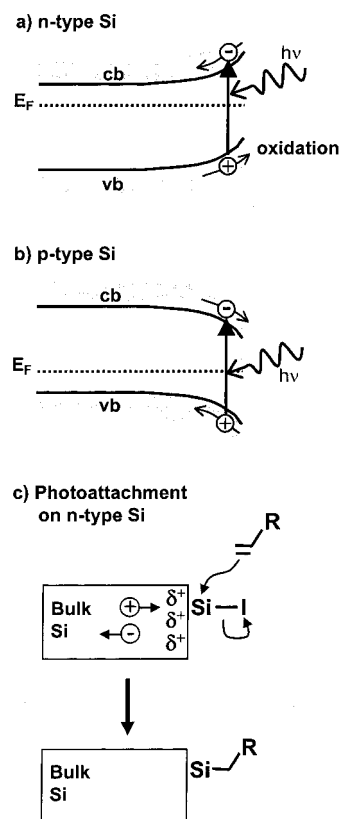


Figure 8. Schematic illustrations of energy bands and photoinduced oxidation and reduction reactions at n-type and p-type silicon surfaces: (a) n-type sample with Fermi level pinned mid-gap; (b) p-type sample with Fermi level pinned mid-gap; and (c) overall illustration of the photoattachment process.

plane (0° angle of incidence), as well as when the electric field vector is almost normal to the surface (p-polarized, 70° angle of incidence). Direct photochemical excitation of the Si–I bond would be expected to be strongly dependent on the relative orientation of the electric field vector of the light and the transition dipole associated with the excitation; by symmetry, this dipole must be either parallel or perpendicular to the Si–I bond axis. The reaction efficiency is also maximized under conditions in which the maximum amount of light is absorbed by the sample.

The above data strongly suggest that the primary mechanism is creation of electrons and holes in the bulk, which are separated by the large electric fields that are typically found in the subsurface space–charge region. This process is illustrated schematically in Figure 8. The I-terminated, n-type silicon samples exhibit upward band-bending near the surface, such that photoexcited electrons drift into the bulk and photoexcited holes drift toward the surface, where they can induce oxidation reactions. The net effect on n-type silicon is to make surface Si atoms more positively charged and therefore susceptible to nucleophilic attack by reactive solution-phase molecules. Conversely, p-type samples (Figure 8b) typically exhibit downward band-bending, such that photoexcited holes drift away from the surface. We propose that the photoattachment process occurs preferentially on n-type Si samples because the band-bending drives the excess minority carriers (holes) toward the surface, making the surface more positively charged and more susceptible to nucleophilic attack by alkenes, as depicted in Figure 8c. Upon steady illumination, the number of photoexcited holes driven toward the surface is determined by the amount of band-bending and by the lifetime of the photoexcited holes. Since

for n-type samples the driving force for the holes to migrate to the surface increases with the dopant concentration, highly doped samples have the highest photoattachment efficiency. This mechanism appears similar to that proposed by Haber et al.¹¹ for the reaction of I-terminated Si surfaces with methanol and is also similar to that proposed for the reaction of iodasilane compounds with methanol.⁸ In each case, the reaction involves nucleophilic attack by an electron-rich species at an electron-deficient $\text{Si}^{\delta+}$ species.

The above mechanism depends critically on whether the semiconductor bands are flat or whether electronic states in the band gap create new electronic states that exchange charges with the bulk and, consequently, induce band-bending in the near-surface region. The existence of band-bending is clearly evidenced from our photovoltaic measurements. In these experiments, the reversal in sign between n-type and p-type samples indicates that the bands on n-type and p-type samples are bent in opposite directions. The ability to bend the bands upward on n-type samples and downward on p-type samples indicates that Fermi level positions are pinned somewhere mid-gap. More quantitative information cannot be extracted from the existing experiments, because the magnitude of the SPV depends on other experimental factors, such as the carrier recombination rate, which are not known for our samples. However, a mid-gap pinning position is also evidenced from XPS binding energies. While most XPS binding energies reported here have been corrected to constant $\text{Si}(2\text{p}_{3/2})$ binding energy of 99.4 eV, the *uncorrected* binding energies show a difference of 0.2 eV between the $0.1 \Omega\cdot\text{cm}$ p-type (acceptor concentration $2.4 \times 10^{17} \text{ cm}^{-3}$) and $0.005 \Omega\cdot\text{cm}$ n-type (donor concentration $1.5 \times 10^{19} \text{ cm}^{-3}$) samples. However, based on the doping values, the difference in bulk Fermi energies is 0.97 eV. If the electron potential energy was constant from the bulk to the surface (i.e., the "flat-band" condition), we would then expect to see a shift of nearly 1.0 eV in the $\text{Si}(2\text{p})$ binding energy of the bulk Si between the highly doped n- and p-type samples. Since the experiments show a shift of only 0.2 eV, we conclude that there must be significant band-bending, which leaves the Fermi level position at the surface pinned at nearly the same position (within ~ 0.2 eV) on n-type and p-type samples.

The mechanism we believe responsible for reaction on I-terminated Si suggests that photoreaction should be possible at all wavelengths short enough to create excitations across the band gap of 1.1 eV. However, we also note that at long wavelengths the electron-hole pairs may be generated very deep in the sample and may therefore not be very effective in causing a photovoltaic effect in the near-surface region. The absorption depth of light in Si decreases monotonically by more than 6 orders of magnitude, from ~ 1 cm to only 100 Å, as the excitation wavelength is decreased from 1 μm to 350 nm.²¹ At 514 nm the absorption depth is ~ 700 nm. As in more conventional semiconductor-liquid interfaces, the only minority carriers (holes, for n-type Si) that are expected to be able to influence the surface photovoltaic effect are those that are created sufficiently close to the surface to be able to diffuse into the near-surface depletion region,²² which for highly doped n-type Si extends only a few hundred angstroms beneath the surface.³² Although the diffusion length will depend on the bulk lifetime and the surface recombination rate (both of which are unknown in our reaction geometry), typical values are on the order of microns. Thus, we expect that shorter wavelengths may be more efficient at excitation because the electron-hole pairs will be generated nearer the surface.

Finally, we note that the mechanism of reaction of I-terminated Si appears to be quite distinct from that of H-terminated Si. In a vacuum, photochemical H removal from Si surfaces occurs with excitation of electrons or photons with energies of >6 eV.^{1,33,34} When in contact with an alkene solution, however, reaction can occur via a radical chain process after initiation at wavelengths shorter than ~ 350 nm (~ 3.5 eV).⁵ However, there is no evidence for reaction of H-terminated silicon with alkenes at wavelengths >350 nm. This may be attributable to a higher bond strength for Si-H. It is clear, however, that the use of iodine-terminated Si presents a new method for chemical photopatterning using visible light.

Conclusions

Our results show that a monolayer of iodine can act as a photolabile passivating agent for chemical modification of silicon surfaces using visible light. The strong doping dependence, in conjunction with the polarization and angle dependence, shows that the mechanism does not involve direct excitation of a Si-I bond, but instead involves excitation of bulk electron-hole pairs and, for n-type silicon, the drift of the photogenerated holes to the surface. The strong dependence of the reaction rate on the doping of the sample suggests that it should be possible to create more complex patterns either through optical masking techniques, or alternatively, by using standard microelectronics methods such as ion implantation to create a spatially modulated doping in the substrate, with subsequent reaction occurring only on the n-type regions. These results represent the first experiments showing the ability to use a single atomic monolayer with visible light to control chemical patterning at a surface.

References and Notes

- (1) Avouris, P.; Walkup, R. E.; Rossi, A. R.; Shen, T.-C.; Abeln, G. C.; Tucker, J. R.; Lyding, J. W. *Chem. Phys. Lett.* **1996**, *257*, 148–154.
- (2) Bevinton, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill Book Company: New York, 1992.
- (3) Buriak, J. M. *Chem. Commun.* **1999**, 1051–1060.
- (4) Cai, W. Unpublished work University Of Wisconsin-Madison, 2001.
- (5) Cicero, R. L.; Linford, M. R.; Chidsey, C. E. D. *Langmuir* **2000**, *16*, 5688–5695.
- (6) Colaianni, M. L.; Chen, P. J.; Gutleben, H.; Yates, J. T., Jr. *Chem. Phys. Lett.* **1992**, *191*, 561–568.
- (7) Collier, C. P.; Wong, E. W.; Belohradsky, M.; Raymo, F. M.; Stoddar, J. F.; Kuekes, P. J.; Williams, R. S.; Heath, J. R. *Science* **1999**, *285*, 391–394.
- (8) Eaborn, C.; Safe, K.; Ritter, A.; Binder, W. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1397–1401.
- (9) Effenberger, F.; Gotz, G.; Bidlingmaier, B.; Wezstein, M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2462–2464.
- (10) Graf, D.; Bauer-Mayer, S.; Schnegg, A. *J. Vac. Sci. Technol. A* **1993**, *11*, 940–944.
- (11) Haber, J. A.; Lauermann, I.; Michalak, D. J.; Vaid, T. P.; Lewis, N. S. *J. Phys. Chem. B* **2000**, *104*, 9947–9950.
- (12) Hofer, W. A.; Fisher, A. J.; Lopinski, G. P.; Wolkow, R. A. *Phys. Rev. B* **2001**, *63*, 85314.
- (13) Horanyi, T. S.; Pavelka, T.; Tutto, P. *Appl. Sur. Sci.* **1992**, *63*, 306–311.
- (14) Kar, S.; Miramond, C.; Vuillaume, D. *Appl. Phys. Lett.* **2001**, *78*, 1288–1290.
- (15) Kelley, S. O.; Jackson, N. M.; Hill, M. G.; Barton, J. K. *Angew. Chem. Int. Ed.* **1999**, *38*, 941–945.
- (16) Kurita, K.; Shingyouji, T. *Jpn. J. Appl. Phys.* **1999**, *38*, 5710–5714.
- (17) Linford, M. R.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1993**, *115*, 12631–12632.
- (18) Linford, M. R.; Fenter, P.; Eisenberger, P. M.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1995**, *117*, 3145–3155.
- (19) MacPherson, C. D.; Hu, D. Q.; Leung, K. T. *Solid State Commun.* **1991**, *80*, 217–220.
- (20) Meyer zu Heringdorf, F.-J.; Reuter, M. C.; Tromp, R. M. *Nature* **2001**, *412*, 517–520.

- (21) *Handbook of optical constants of solids*; Palik, E. D., Ed.; Academic Press: Orlando, 1985.
- (22) Pleskov, Y. V.; Gurevich, Y. Y. *Semiconductor Photoelectrochemistry*; Consultant's Bureau: New York, 1986.
- (23) Rakitin, A.; P, P. A.; Papadopoulos, C.; Kobzar, Y.; Vedenev, A. S.; Lee, J. S.; Xu, J. M. *Phys. Rev. Lett.* **2001**, *86*, 3670–3673.
- (24) Royea, W. J.; Michalak, D. J.; Lewis, N. S. *Appl. Phys. Lett.* **2000**, *77*, 2566–2568.
- (25) Schlaf, R.; Hinogami, R.; Fujitani, M.; Yae, S.; Nakato, Y. *J. Vac. Sci. Technol. A* **1999**, *17*, 164–169.
- (26) Schön, J. H.; Berg, S.; Kloc, C.; Batlogg, B. *Science* **2000**, *287*, 1022–1023.
- (27) Sieval, A. B.; Demirel, A. L.; Nissink, J. W. M.; Linford, M. R.; Maas, J. H. v. d.; Jeu, W. H. d.; Zuilhof, H.; Sudhölter, E. R. J. *Langmuir* **1998**, *14*, 1759–1768.
- (28) Stephens, A. W.; Green, M. A. *Solar Energy Mater. Solar Cells* **1997**, *45*, 255–265.
- (29) Strother, T.; Cai, W.; Zhao, X.; Hamers, R. J.; Smith, L. M. *J. Am. Chem. Soc.* **2000**, *122*, 1205–1209.
- (30) Strother, T.; Hamers, R. J.; Smith, L. M. *Nucleic Acids Res.* **2000**, *28*, 3535–3541.
- (31) Sundarababu, G.; Gao, H.; Sigrist, H. *Photochem. Photobiolog.* **1995**, *61*, 540–544.
- (32) Sze, S. M. *Physics of Semiconductor Devices*; J. Wiley: New York, 181.
- (33) Vondrak, T.; Zhu, X. *J. Physical Chem. B* **1999**, *103*, 4892–4899.
- (34) Vondrak, T.; Zhu, X.-Y. *Phys. Rev. Lett.* **1999**, *82*, 1967–1970.
- (35) Wagner, P.; Nock, S.; Spudich, J. A.; Volkmuth, W. D.; Chu, S.; Cicero, R. C.; Wade, C. P.; Linford, M. R.; Chidsey, C. D. E. *J. Struct. Biol.* **1997**, *119*, 189–201.