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Molecularly Controlled Modulation of Conductance on Azobenzene Monolayer-Modified Silicon Surfaces

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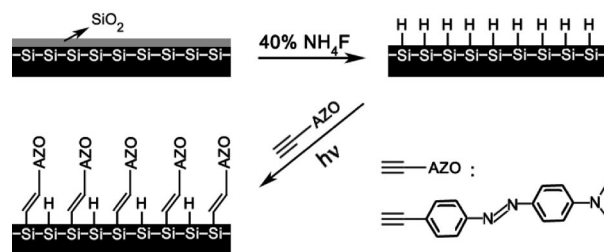
Controlled modulation of silicon surface properties is of great importance for the development of silicon-based molecular electronic devices because of the ubiquitous role of silicon in microelectronics. In this article, photoresponsive azobenzene molecules were covalently grafted onto hydrogen-terminated Si(111) surfaces via Si–C linkages. These direct Si–C bond linkages are preferred over Si–O linkages at the interfaces because of the higher stability and the better electronic continuation between Si and the alkyl chain. The modified surfaces were characterized by X-ray photoelectron spectroscopy (XPS) and attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. The reversible photoisomerization effects of the azobenzene molecules were also studied with contact angle measurements, atomic force microscopy (AFM), and conductive atomic force microscopy (C-AFM). The measured conductivity showed a reversible switching behavior by alternate illumination with UV and visible light. Thus, we have demonstrated molecularly controlled modulation of conductance of the Si surface by the photochemical method. Furthermore, the dipole moments of the azobenzene molecules switched accordingly with the alternate illumination. Making use of this characteristic, we have provided a strategy to evaluate the influence of the molecular dipole moments on the conductance of the semiconductor surface.

1. Introduction

With the advent of molecular electronics, it is essential to understand thoroughly the influence of the electronic states of molecules and the molecular aggregate interface on the charge transport character.^{1–4} Studies have shown that electronic transport through devices depends critically on the properties of the interfaces through which electrons pass, which is controlled by the interface dipoles and the density and energy distribution of the surface state.^{1,5,6} So, it is attractive to seek controllable modulation of device performance through surface modifications. For which, grafting molecular properties onto metals or semiconductors is an important research approach, which allows the use of the cooperative properties of these solids and the controllable functional versatility of molecules.⁶ Over the past decade, researchers have established many different molecule/metal or molecule/semiconductor hybrid systems to learn the impact of interface dipole on the charge transport character. In those studies, series of molecules with different dipole moments were used to regulate the electrical properties of the solid surfaces by introducing π -electron-donating or π -electron-withdrawing functional groups.^{2,7–9}

In recent years, considerable attention has been paid to the research of covalent attachment of organic monolayers to hydrogen-terminated silicon surfaces.^{10–12} Interest in this area is driven by the opportunity to combine the advantages of Si in microelectronics with versatile functionalities of organic molecules. Such silicon surfaces, without the thin native interfacial

SCHEME 1: Scheme for the Preparation of Covalently Attached DMAEAB Monolayer on the Si(111) Surface



silicon oxide layer, may have great potential in the development of hybrid molecule/semiconductor electronic devices and bio-compatible devices.¹⁰

In this article, a novel photoresponsive azobenzene-containing molecule, 4-*N,N*-dimethylamino-4'-ethynyl-azobenzene (DMAEAB), with an end alkyne group as the binding unit, has been synthesized and grafted directly on hydrogen-terminated Si(111) surfaces through light-promoted hydrosilylation (Scheme 1). These direct Si–C bond linkages are preferred over Si–O linkages at the interfaces because of the higher stability^{13,14} and the better electronic continuation between Si and the alkyl chain.^{15–17} The DMAEAB-modified surfaces were characterized by XPS and ATR-FTIR spectroscopy, and the reversible photoisomerization effects of azobenzene molecules were confirmed with water contact angle measurements, AFM, and C-AFM. The measured conductivity showed a reversible switching behavior by alternate illumination with UV and visible light, which provides a promising method to manipulate the chemical and physical properties of silicon surfaces.

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To evaluate the influence of the molecular dipole moments on the conductance of semiconductor surfaces, many researchers have compared the conductance among surfaces grafted with molecules of different dipole moments, but it is difficult to guarantee that their monolayer coverage is identical. Our method using azobenzene molecules whose dipole moments can be switched with UV and visible light illumination could effectively eliminate the influence of the monolayer coverage differences and makes the comparison more reliable and persuasive.^{2,7–9} Thus, this work provides an effective strategy to evaluate the influence of the molecular dipole moment on the surface conductance, which will be of great importance for molecular or nanodevices based on molecularly modified Si surfaces.

2. Experimental Section

2.1. Chemicals and Materials. The compound DMAEAB was prepared according to literature procedures.^{18,19} Mesitylene (Aldrich, 98%) was redistilled from sodium under vacuum and stored over molecular sieves. Analytical-grade chemicals were used for cleaning (30% H₂O₂, 98% H₂SO₄) and etching (40% NH₄F solution) pieces of silicon wafers. Other reagents were purified according to the standard methods before being used. The solution was deoxygenated with dry nitrogen for at least 1 h. The Si(111) crystal was n-type phosphorus doped with 0.008–0.02 $\Omega \cdot \text{cm}$ resistivity.

2.2. Preparation of DMAEAB-Modified Si(111) Surfaces. Si(111) samples were cleaned ultrasonically in acetone followed by methanol (5 min each time). The clean silicon wafers were oxidized in 3:1 (v/v) concentrated H₂SO₄/30% H₂O₂ for 1 h at 100 °C and then rinsed thoroughly with ultrapure water (resistivity >18 M $\Omega \cdot \text{cm}^{-1}$). The oxidized samples were then immersed in a deoxygenated 40% aqueous NH₄F solution for 5 min to remove the oxide layer. The samples were then rinsed with ultrapure water and were blown dry under nitrogen flow after each step. For Si(111), it is known that atomically flat hydrogen-terminated silicon surfaces could be prepared by this etching process.^{20–23}

It has been possible to prepare the monolayer-modified silicon surfaces by the thermal,²⁴ catalyzed,²⁵ radical-initiated,²⁶ electrochemical,²⁷ or photochemical reactions²⁸ with hydrogen-terminated Si surfaces. In this study, the photochemical method was carried out. A solution (0.1 M) of DMAEAB in mesitylene was flushed with Ar for at least 30 min before the freshly etched hydrogen-terminated Si(111) samples were added. Then, the quartz vessel containing the samples was sealed and purged continuously with a small flow of dry Ar and was illuminated with a high-pressure mercury vapor lamp (400 W). After illumination for 2.5 h, the samples were removed from the solution, and the surface was rinsed with deoxygenated CH₂Cl₂ to remove any physisorbed species.

2.3. Reversible Photoisomerization Effect of DMAEAB-Modified Si(111) Surfaces. Azobenzene compounds are typical materials displaying reversible photoisomerization effects: under UV irradiation, azobenzene compounds convert from the thermodynamically stable trans form to the cis form, and by visible light irradiation or heating, the cis form azobenzene can revert to the trans form. Accordingly, significant changes in physical properties such as dipole moment, polarizability, and refractive index would occur.^{29–31} To demonstrate the photoisomerization effects, we alternately irradiated DMAEAB-modified surfaces with UV and visible light. The measured light intensity at the sample was 8.2 mW cm^{−2} for UV light centered at 365 nm and 20.0 mW cm^{−2} for visible light centered at 450 nm. The isomerization effects were studied by water contact angle, morphology, and electrical conductivity characterization.

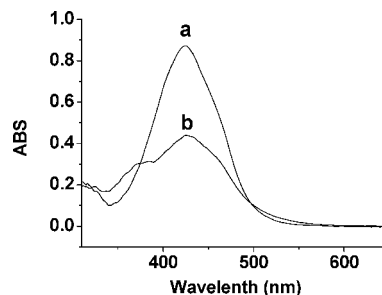


Figure 1. Absorption spectra of the compound DMAEAB in 10^{−5} M mesitylene solution after illumination with visible light for 120 s (a) and UV light for 60 s (b).

2.4. Characterization Techniques. Contact angle measurements were taken with an OCA20 contact angle system (DataPhysics, Germany) at ambient temperature. For static contact angle (θ_s), a 5 μL drop of water was used.

X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab250 electron spectrometer from Thermofisher using 150W Al K α radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C 1s line at 284.6 eV from adventitious carbon.

The attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra of the monolayers were obtained on a Nicolet-8700 spectrometer in a multiple internal reflection mode, and a freshly prepared hydrogen-terminated Si(111) was taken as the background. An ATR accessory of ZnSe crystal and incidence angle of 65° was utilized. All spectra were taken using a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector with an instrument resolution of 4 cm^{−1} and averaging 1000 scans. During data acquisition, the measurement chamber and ATR accessory were purged with dry N₂.

UV–vis spectra of the solution were recorded on a Hitachi U4100 spectrophotometer. Atomic force microscopy (AFM) characterization was performed with an SPI 3800N multimode scanning probe microscope (Seiko Instruments). Topographical images were obtained in contact mode with a silicon cantilever having a nominal spring constant of 0.02 N/m and at a scan rate of 0.50–1.0 Hz. *I*–*V* curves were measured with conductive atomic force microscopy (C-AFM) using a gold-coated silicon cantilever under ambient conditions.

3. Results and Discussion

3.1. Formation of DMAEAB Monolayers on Si(111) Surfaces. Figure 1 shows the changes of absorption spectra of the compound DMAEAB in 10^{−5} M mesitylene solution by alternate illumination with UV light centered at 365 nm and visible light centered at 450 nm. As shown in Figure 1a, the strong intensity peak at 424 nm is due to π – π^* electronic transition. Upon UV irradiation for 60 s, the intensity of the π – π^* transition decreased (Figure 1b), which can be attributed to the trans-to-cis isomerization.^{29–31} Then, the reverse isomerization was induced by irradiation of the solution with visible light for 120 s. On further alternate illumination with UV and visible light, the spectrum changed between curve a and b. It is known that cis form of azobenzene molecules occupies larger free volume than trans form. To ensure the photochemical isomerization of the azobenzene molecules with enough molecule free volume, we grafted alkyne-ended DMAEAB molecules onto the Si(111) surfaces under UV irradiation. The UV light not only activates surface chemical modification, but also converts the

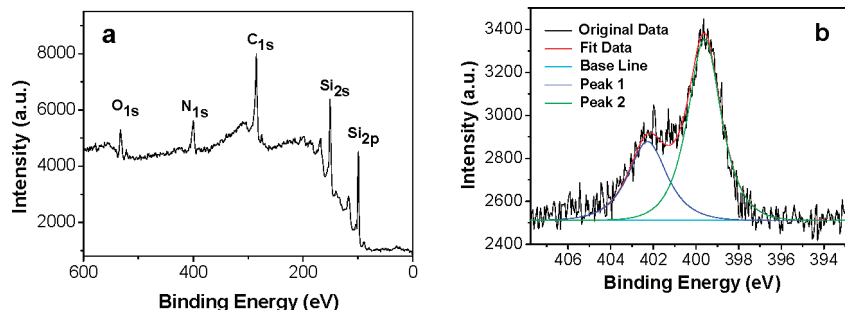


Figure 2. XPS spectra for the compound DMAEAB modified Si(111) surface. (a) A survey spectrum. (b) High-resolution XPS spectrum of the N_{1s} region and the fitted result.

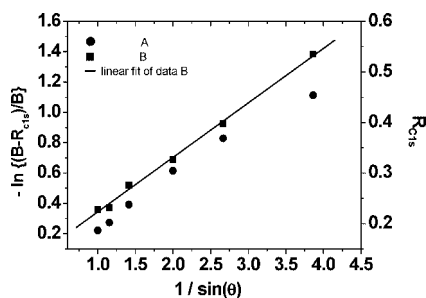


Figure 3. Coverage evaluating by data processing of the angle-resolved XPS C_{1s} measurements on DMAEAB-modified Si(111) and on HOPG.

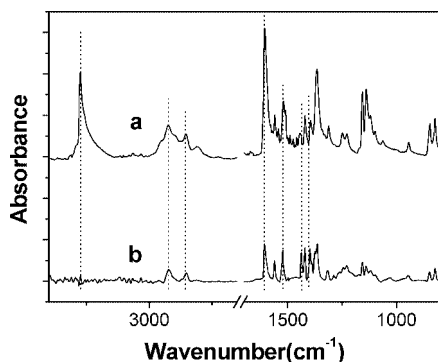


Figure 4. IR spectrum of the solid DMAEAB in a KBr pellet (a) and the ATR-FTIR spectrum of the DMAEAB monolayer grafted on the Si(111) surface (b).

molecular configuration from trans to cis form, which would increase the free volume of the molecules.^{32,33}

3.2. Water Contact Angle Characterization of Isomerization Effect. The quality of the monolayer of DMAEAB grafted on Si(111) can be evaluated by the water contact angle measurements.^{34,35} After 2.5 h of grafting reaction and the processing procedures, the maximum contact angles of the azobenzene monolayer arrived at $89.4 \pm 1.2^\circ$. The reversible isomerization effect of the DMAEAB monolayer was confirmed directly by contact angle measurements. Upon UV irradiation for 60 s, the molecular configuration change of DMAEAB from trans to cis form resulted in a change in water contact angle from $89.4 \pm 1.2^\circ$ to $82.3 \pm 1.7^\circ$. After visible light irradiation for 120 s, a completely reversion was realized. The reversible contact angle change can be attributed to the azobenzene isomers' difference on Si(111) surfaces.³⁶ This process was repeated several times, and good reversibility of the surface wettability was observed.

3.3. XPS Spectra of DMAEAB Monolayers on Si(111) Surfaces. Surface species grafted on Si(111) surfaces were identified chemically using XPS measurement. Figure 2 shows

TABLE 1: Assignment of the Major IR Absorption Peaks of DMAEAB Film and in Bulk^{18,19,41,42}

peak assignment	monolayer (cm ⁻¹)	bulk (cm ⁻¹)
ν_{CH}		3273
ν_{phenyl}	1605, 1522	1602, 1516
$\nu_{\text{phenyl-NN}}$	1140	1137
$\nu_{\text{N-(CH}_3)_2}$	1247	1247
ν_{CH_3}	2924, 2854	2922, 2852
$\nu_{\text{N=N}}$	1420	1418

the XPS spectra in the regions of the silicon (2p), carbon (1s), nitrogen (1s), and oxygen (1s), collected from the DMAEAB-modified Si surfaces. As can be seen, in addition to the peaks of Si_{2s} and Si_{2p} due to substrate Si(111), the spectrum exhibits peaks of N_{1s} and C_{1s}, and the relative intensity of the two peaks is 1:6.2, which is roughly in agreement with the ratio of 3:16 for the DMAEAB monolayer on the Si(111) surface. The experiment spectrum (black line) of the N_{1s} is deconvoluted into two peaks centered at 399.3 eV (green line, 67%), and 402.1 eV (blue line, 33%) comprising the combined signal (red line) with an area ratio of 2:1 (Figure 2b), which are associated with N=N and N-C bonds, respectively, in good agreement with the N atom ratio in the DMAEAB molecules.^{37,38} Very little signal at about 532.5 eV is observed, demonstrating that a small amount of silicon oxide exists.

3.4. Evaluation of Coverage and Thickness of the Monolayer. The coverage and thickness of the monolayer were evaluated by angle-resolved XPS according to the method reported by Wallart³⁹ and Fadley.⁴⁰ The volume density of carbon atoms $\rho_{\text{C,ML}}$ and film thickness d can be determined through the angle-resolved study of the C_{1s} signal on the modified silicon surface and on a reference sample, highly ordered pyrolytic graphite (HOPG). As shown in Figure 3, the dots show the C_{1s} peak relative intensity R_{C1s} (C_{1s} peak intensity at the DMAEAB modified Si(111) surface divided by the C_{1s} peak intensity at HOPG surface) versus $1/\sin(\theta)$ for the selected polar angle $\theta = 15^\circ, 22^\circ, 30^\circ, 45^\circ, 60^\circ$, and 90° , whereas the squares show the $-\ln\{(B - R_{\text{C1s}})/B\}$ values versus $1/\sin(\theta)$ for the six polar angles (B is a parameter related to the carbon density $\rho_{\text{C,ML}}$).³⁹ The solid black line represents the best linear fit derived from the square data, through which we can calculate out the carbon density $\rho_{\text{C,ML}} = 3.19 \times 10^{20} \text{ cm}^{-3}$ and monolayer thickness $d = 1.37 \text{ nm}$, and the surface coverage $\theta_{\text{ML}} = 0.35$ for $n = 16$ through the equation $\theta_{\text{ML}} = \rho_{\text{C,ML}} d/n/D_{\text{Si}}$ (ref 35 eq 13, n is the number of carbon atoms, and $D_{\text{Si}} = 7.8 \times 10^{14} \text{ cm}^{-2}$ is the surface atom density on Si(111)).

3.5. ATR-FTIR Spectra of the DMAEAB Monolayers on Si(111) Surfaces. The surface chemistry of the grafted organic monolayer was characterized further by ATR-FTIR spectrum, and the IR spectrum of a solid sample (powdered in KBr) of the parent compound is shown in the top trace for comparison.

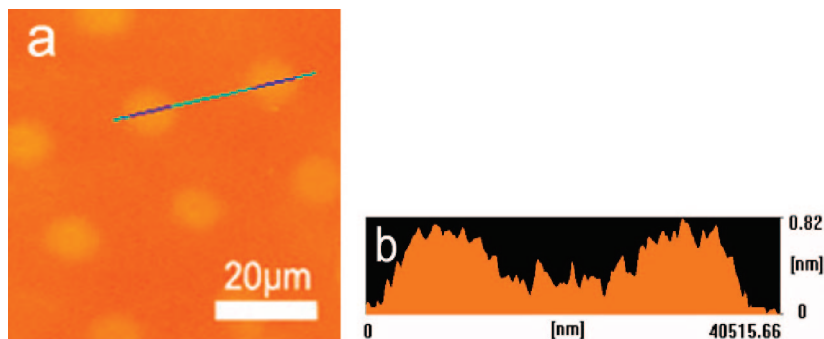


Figure 5. AFM images of the DMAEAB molecule's modified Si(111) surface. (A) Topographical image after UV illumination through a mask; (B) cross section of the solid line in (A).

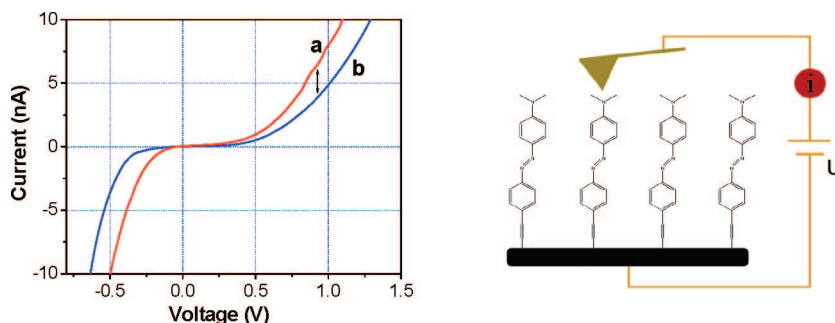


Figure 6. (A) Typical I - V characteristics for trans- (curve a) and cis-form (curve b) DMAEAB monolayer grafted on Si(111) surfaces. The curves are averages from five different experimental locations on the surface. (B) Schematic diagram of measurement system.

Comparison of the IR spectra of the solid and monolayers shown in Figure 4 reveals that the band at 3273 cm^{-1} due to the ν_{CH} vibration is clearly absent from the spectrum of the monolayer, which is evidence of the grafting of molecules by alkyne substitution.⁴¹ One can clearly see the presence of absorption peaks of aromatic ring C=C bond vibrations, aniline aromatic C-N stretching vibrations, aniline aliphatic C-N stretching vibrations, and the C-H stretching vibrations of $-\text{N}(\text{CH}_3)_2$ groups in the IR spectra of both monolayer and solid forms (see Table 1).^{18,19,42} In spite of certain differences (such as much broader lines in the monolayer and somewhat different relative intensity) in other absorption regions, the IR spectrum of DMAEAB in the monolayer is very similar to that of the solid samples, which confirms that we have grafted DMAEAB molecules on the Si(111) surface successfully.

3.6. Stability of Monolayers on Si(111) Surfaces. The stability of the DMAEAB monolayer was tested through IR²⁰ and contact angle measurements.¹⁴ Studies showed that the IR spectra showed no obvious changes after storing the sample in laboratory ambient conditions for 10 days, and no distinct difference in wettability was observed for the trans- and cis-state monolayer during that period of time, which demonstrated that not only the grafted monolayer was stable but also the isomerization performance of the azobenzene molecules was reproducible. Furthermore, after the sample was kept in boiling water for 1 h, no distinct loss of intensity was observed in the IR spectra. These results showed the favorable stability of the DMAEAB monolayer in contrast to the monolayer prepared in our previous work³⁰ with the binding strategy of Si-O-C, where the IR intensity of the monolayer decreased markedly after it suffered to the same treatment.

3.7. Topographical Character of Isomerization Effect of the DMAEAB Monolayer Si(111) Surface. The DMAEAB molecules modified on Si(111) surfaces can be reversibly switched between the trans and cis configuration under two different wavelength lights.²⁹⁻³¹ In this work, the DMAEAB-

modified Si(111) surface was pressed against a photomask, a grid with ca. $10\text{-}\mu\text{m}$ -diameter gold spots and a center-to-center spacing of ca. $15\text{ }\mu\text{m}$. The surface was then exposed through the mask to 365-nm light for 5 min. Then the mask was removed and the reversible topography change of the Si(111) surface on alternate illumination with UV and visible light was investigated with AFM. The results indicate that the AFM image of the surface before UV illumination displays a flat surface. After UV illumination through the mask, a number of hills are observed on the surface (Figure 5a). The average height of the hills is about 0.65 nm (see cross section in Figure 5b), which is associated with height change formed during the trans-to-cis transform process, indicating that only DMAEAB molecules on unmasked regions of the Si(111) surface, that is, parts of the surface exposed to the light, are transformed from trans to cis form, whereas the masked regions retain trans form. These hills almost disappeared on illumination with visible light, and the morphological change was reversibly observed by the alternate illumination with UV and visible light.

3.8. Electrical Character of Isomerization Effect of the DMAEAB-modified Si(111) Surfaces. The understanding and control of electrical properties of silicon surfaces are of great importance for the fabrication of silicon-based molecular electronic devices.¹⁰⁻¹² For which, the current-voltage (I - V) characteristics of the Si(111) surface modified with DMAEAB in our present study were assessed by probing the Si(111) surfaces with C-AFM (Figure 6). From Figure 6, we can see that the surface shows a different conductive characteristic when DMAEAB molecules grafted on the silicon surface are in different molecular conformations. For the surface grafted with trans-configuration DMAEAB molecules, the current is higher than that of the cis configuration at the same voltage conditions. As an example, at the voltage -0.30 V , the current ratio arrives at a value of 6. With alternate illumination of the surface with UV and visible light, the reversible conductance of the DMAEAB-modified Si(111) surface occurred. In 10 cycles, the

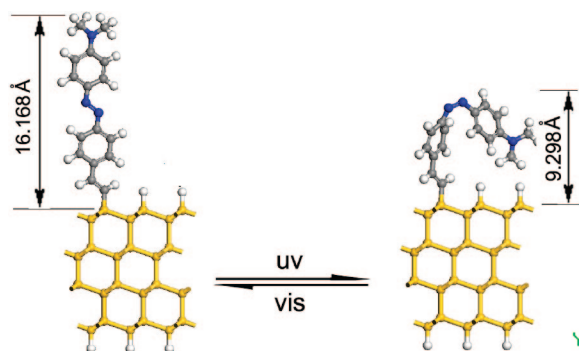


Figure 7. The side view of the trans- and cis-conformation DMAEAB molecule grafted on silicon substrate (optimized with MM+ force field) and the reversible photoisomerization transformation process.

conductive characteristic shows good reproducibility. Thus, on the basis of the photoinduced conformation change of DMAEAB molecules, the electrical behavior of the modified Si(111) surface can be well-controlled. During I - V measurements, the same tip was used, and the samples were under dark conditions to avoid the effect of illumination on DMAEAB molecules isomerization. For more accuracy, the typical I - V curves were attained in a statistic manner. This result indicates that we could construct an optical stimulated and electrical feedback molecular electronic devices based on such hybrid systems.

It is known that there is a strong dependence of charge transport on the dipole of the molecular layer.^{2,7-9} To reveal in a clearer way the effects of dipole on charge transport, we carried out molecular mechanics (MM) simulations to study the packing structures and the interface dipole of DMAEAB molecules on a large silicon (8×6) matrix. On the basis of experimental results, surface models with $1/3$ coverage ratio are constructed in our simulations. Two configurations, *cis*- and *trans*-DMAEAB, are considered. The optimized unit cell structures are shown in Figure 7. The results indicate that the trans isomer is characterized by a planar structure, but in the cis isomer the benzene aromatic rings are twisted with each other. The optimized height of the trans isomer is 1.6168 nm, which has some difference with the calculated monolayer thickness $d = 1.37$ nm. In fact, the d value calculated from angle-resolution XPS experiments means the distance between the top carbon atom and the bottom carbon atom of the trans isomer, it is comparable with the optimized height of the trans isomer after adding the bond length of the top bond C-H and the bottom bond C-Si. The length disparity of optimized trans and cis isomers is 6.87 Å, which is consistent with the AFM experimental result (Figure 5b). The effective dipole (perpendicular to the Si (111) surface) of the trans-form DMAEAB molecules points downward, whereas that of the cis isomer points upward. The disparity value of the effective dipole moment is 2.4 D. It is just this difference of dipole moments that has led to the change of the electrical properties of surface drastically.²

Conclusions

A novel azobenzene molecule with an end alkyne group as the binding unit has been synthesized and covalently grafted onto Si(111) surfaces by irradiating a hydrogen-terminated silicon wafer with UV light. By combinatory measurements of water contact angles, XPS, AFM, and ATR-FTIR spectroscopy, it was shown that high-quality monolayers have been fabricated, and the reversible photoisomerization effect has been demonstrated with contact angle measurements, AFM and C-AFM on

such surfaces. The influence of the different dipole moments of DMAEAB molecules isomers on the Si(111) surface conductance has been demonstrated and simulated. With such surfaces, the electrical property could be modulated by alternate irradiation with UV and visible light due to the conversion of DMAEAB between trans and cis form. The electrical sensitivity of the isomers to the illumination may be exploited to identify them using electrical transport measurements and would offer an approach to construct novel photoresponsive intelligent silicon surfaces. This study can also be extended to other optical, electrical switching molecular systems, which would be of great importance for the development of Si surface-based optical-electrical molecular devices.

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Supporting Information Available: The synthesis procedure of the compound DMAEAB. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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