

# Photochemical-Controlled Switching Based on Azobenzene Monolayer Modified Silicon (111) Surface

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Azobenzene-containing compounds were covalently attached onto Si(111) surfaces via Si–O linkages using a two-step procedure. The modified Si(111) surfaces were characterized by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FT-IR) spectroscopy measurements. The monolayer surface showed preferably chemical stability. Switchable photoisomerizability of azobenzene molecules on these modified surfaces was observed in response to alternating UV and visible light exposure. The measured conductivity showed distinct difference with trans and cis forms of azobenzene compounds on as-modified Si(111) surfaces.

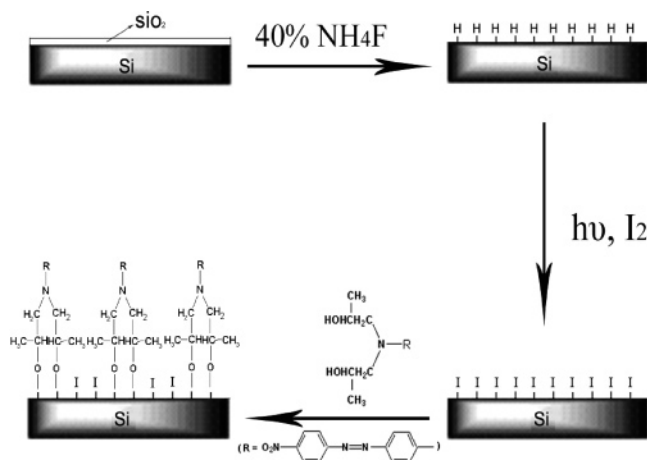
## 1. Introduction

Controlled modification of surface properties is a key feature in the development of chemically based nanotechnology.<sup>1</sup> Recently, particular attention has been paid to the chemical reactivity of hydrogen-terminated silicon surface for both fundamental studies and applications because of the technological importance of silicon in microelectronics,<sup>2</sup> where the organic molecules were directly attached to silicon surfaces by initiating the surface reactions with light, heat, or radical initiators via the formation of Si–C, Si–N, and Si–O bonds.<sup>3–12</sup> Such silicon surfaces covalently bonded with organic monolayer, without the interfacial silicon oxide layer, are quite stable under a variety of conditions,<sup>1</sup> which is important for a detailed physical investigation of the surface properties and developing stable hybrid molecular/semiconductor devices.<sup>13</sup>

Azobenzene and its derivatives have been studied with immense interest for their unique photoisomerization effect.<sup>14–21</sup> The transition from the thermodynamically more stable trans to cis conformation can be induced upon irradiation with UV light and reversed upon heating or irradiation with visible light. From these characteristics, azo molecule is promising for potential technological applications such as photoswitching and storage materials,<sup>14,15,18</sup> photoactive biomaterials,<sup>19</sup> diffractive optical elements,<sup>20</sup> and so forth.

In this paper, an azobenzene-containing compound, 4-nitro-4'-N,N-di(2-hydroxy propyl)aminoazobenzene (NHPA), was synthesized and attached to Si(111) surface (Scheme 1) through Si–O bonds. The molecules chosen for this study contain strong donor and acceptor groups and  $\pi$ -conjugated orbitals, making them suitable for molecular electronics applications. Two hydroxyl groups in the molecules were designed to form Si–O bonds. The modified surfaces were characterized by the analysis of X-ray photoelectron spectroscopy (XPS) and FT-IR spectrum. Reversible photoisomerization effect and the corresponding

SCHEME 1: A Schematic of Monolayer Formation of NHPA Molecules on Silicon Surface via Si–O Bonds



conductive characteristic of the modified Si(111) surface with two kinds of isomers of NHPA molecules were studied at ambient conditions. The measured conductivity showed distinct difference with the trans and cis forms of azobenzene compounds on as-modified Si(111) surfaces. These results indicated the exciting technological possibility to realize photocontrolled electronic process on a functional molecule-modified Si surface.

## 2. Experimental Section

**2.1. Materials.** The compound NHPA was prepared according to the literature procedures.<sup>21</sup> All 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 0.02  $\Omega$ ·cm resistivity.

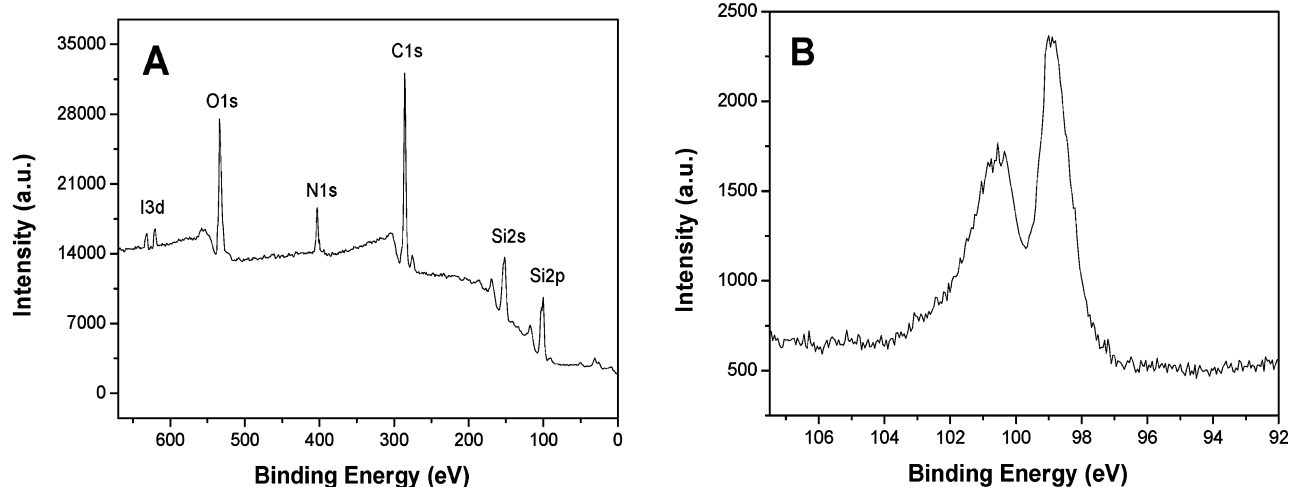
**2.2. Preparation of Oxidized Silicon and Hydrogen-Terminated Surfaces.**<sup>22–25</sup> Si(111) samples were first ultrasonically cleaned in acetone followed by methanol (5 min each) and then were oxidized in 3:1 concentrated H<sub>2</sub>SO<sub>4</sub>/30% H<sub>2</sub>O<sub>2</sub> for 2 h at 100 °C. The oxidized samples were then immersed

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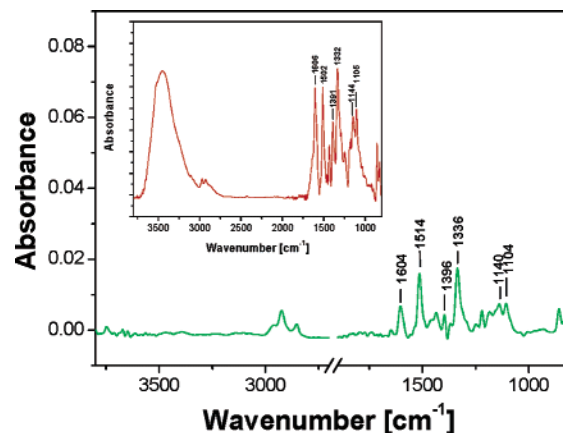
**Figure 1.** XPS spectra of the (A) NHPA monolayer attached on Si(111) and (B) high-resolution XPS spectra of the Si<sub>2p</sub> region of the same sample. The peak of binding energy at about 100.6 eV is mostly due to the Si–O and Si–I bonds. The sample was oriented with a 15° photoelectron takeoff angle from the sample surface to the analyzer.

in a nitrogen-sparged 40% aqueous NH<sub>4</sub>F solution for 5 min. The silicon was rinsed thoroughly with deionized water and was blown dry under a stream of nitrogen gas after each step. For Si(111), this etching condition was known to create a well-ordered monohydride silicon surface.

**2.3. Preparation of Iodine and NHPA-Terminated Si Surfaces.** There have been many previous reports on attaching alcohols to hydride-passivated Si surfaces via Si–H bond cleavage to form Si–O linkages.<sup>22,26–29</sup> It is believed that the direct interaction of alcohol with H-terminated Si(111) occurs with defects on the surface, while halide-modified Si surfaces can afford superior attachment of organic molecules because of the enhanced lability of the Si–X (X = Cl, Br, I) bond relative to the Si–H bond.<sup>12,29</sup> In our present studies, the attachment to hydride-modified surfaces was explored in a two-step strategy.<sup>12,22</sup> First, the hydride-passivated Si(111) surfaces were treated with a saturated solution of I<sub>2</sub> in anhydrous benzene. The solutions were sparged with dry N<sub>2</sub> in a sealed container and were allowed to react with the surface for 20 min at 100 °C. The iodine-terminated silicon sample was then immersed into the solution of NHPA dissolved in purified toluene for the second step reaction. Pyridine was used for the catalyst, which was known to not only facilitate the reaction but also to improve film quality.<sup>22,30</sup> The cell containing the sample was sealed and purged continuously with a small flow of dry Ar and was illuminated with a high-pressure mercury vapor lamp (500 W for 6–8 h). Here, UV light was used to activate surface chemical modification as well as to transform the NHPA molecular configuration from trans to cis form before attachment. Such transformation is helpful for increasing the free volume for conformational change.<sup>31</sup> After each step, the sample was ultrasonically cleaned under dry Ar purge to remove any physisorbed species.

**2.4. Photochemical Switching of the NHPA-Modified Si(111) Surfaces.** Azobenzene compounds are typical materials displaying a reversible photoisomerization effect: UV irradiation causes a trans-to-cis isomerization, and exposure to visible light or heat causes the reverse configurational transition.<sup>31</sup> To demonstrate the modification result, NHPA-modified surfaces (after ultrasonically cleaning and leaving at ambient conditions for more than 24 h) were irradiated by a xenon lamp (500 W) using filters centered at  $\lambda = 365$  nm for UV light and centered at  $\lambda = 450$  nm for visible light.

**2.5. Characterization Techniques.** Contact angle measurements were taken with an OCA20 contact angle system



**Figure 2.** ATR FT-IR spectrum of Si(111) surface after modified with NHPA molecule. Inset: FT-IR spectrum of NHPA in KBr disk. The data are the absorbance produced by 10 reflections in the ATR crystal.

(DataPhysics, Germany) at ambient temperature. For static contact angle ( $\theta_s$ ), a 5- $\mu$ L drop of water was used.

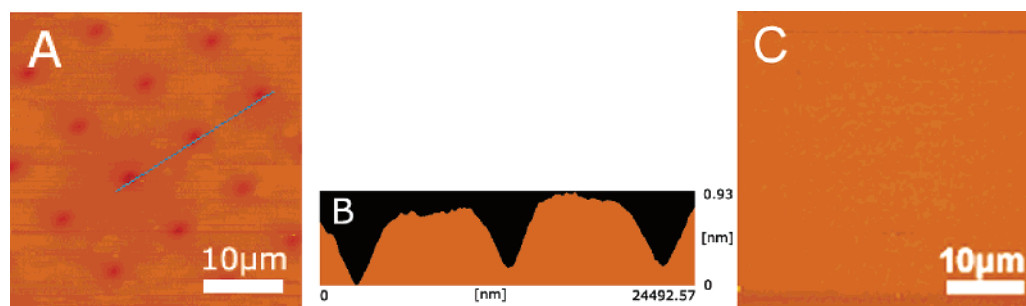
X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al K $\alpha$  radiation. The base pressure was about  $3 \times 10^{-9}$  mbar. The binding energies were referenced to the C<sub>1s</sub> line at 284.6 eV from adventitious carbon.

Attenuated total internal reflectance (ATR) Fourier transform infrared (FT-IR) spectra were taken on a Bruker-EQUINOX55 spectrometer in a multiple internal reflection mode, and a freshly prepared H–Si(111) was taken as the background to obtain absorbance. All spectra were taken with an instrument resolution of 4 cm<sup>-1</sup>.

Atomic force microscopy (AFM) characterization was performed with an SPI 3800N multimode scanning probe microscope (Seiko Instruments). Topographical images were obtained in tapping mode with a silicon cantilever having a nominal spring constant of 3 N/m and a resonant frequency of 24 kHz at a scan rate of 0.50 Hz. *I–V* curves were measured with a P47 scanning tunneling microscopy (STM) under ambient conditions.

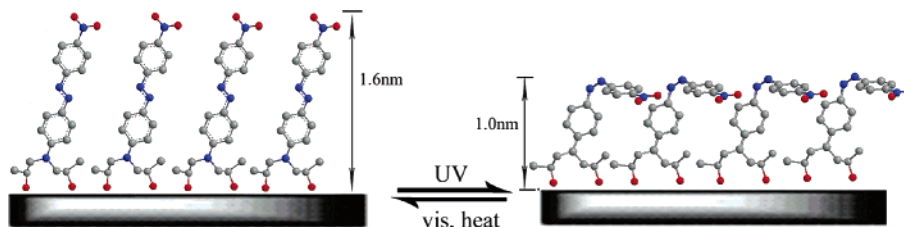
### 3. Results and Discussion

The NHPA-modified Si(111) surface was examined by XPS to determine the surface characteristics for monolayer formation.



**Figure 3.** Contrastive AFM images obtained after irradiation with UV light through a contact mask and subsequent visible light. (A) Topographical image after 30 s UV irradiation, (B) cross section analysis along the solid line in A, and (C) AFM image of the same area as A after succedent 30 s irradiation with visible light.

## SCHEME 2: Photoresponsive Si(111) Surface Prepared by Attaching Azobenzene-Containing Molecules (NHPA) on It<sup>a</sup>



<sup>a</sup> The trans and cis conformation of NHPA was calculated using ChemBats3D Ultra 8.0 molecular modeling analysis software. Atom labels: gray (C), red (O), blue (N); H atoms are omitted.

Figure 1 shows a representative XPS spectrum of as-prepared NHPA-modified Si surface. In Figure 1A, in addition to the bands due to substrate Si, the spectrum exhibits peaks of N<sub>1s</sub> (402.4 eV) and C<sub>1s</sub> (284.6 eV), and the relative intensity of the two peaks is 1:5.5, which is in agreement with the ratio of 1:4.5 for a C<sub>18</sub>H<sub>20</sub>O<sub>3</sub>N<sub>4</sub>O–Si surface species. Additionally, the two peaks at 620.3 and 631.5 eV, corresponding to I<sub>3d5/2</sub> and I<sub>3d3/2</sub>, respectively,<sup>26</sup> still occurs after NHPA-modification, which are attributed to the presence of unreacted Si–I bonds because of the large molecular space volume (Scheme 1). High-resolution XPS spectrum of the Si<sub>2p</sub> shows, in addition to the substrate Si signal (99.0 ± 0.2 eV), a broad peak located at higher ~1.5 eV in binding energy (Figure 1B), the position of which is consistent with the formation of surface Si–O and Si–I bonds.<sup>11,26,32</sup> The peak might also include suboxides, though the wide Si<sub>2p</sub> shoulder band at higher 103.0 eV indicative of SiO<sub>2</sub> is absent.

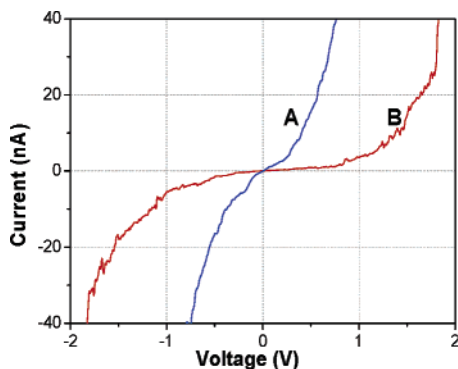
Figure 2 compares the ATR FT-IR spectrum of monolayers formed on Si(111) surface with the transmittance infrared spectrum of NHPA dispersed in KBr.<sup>33</sup> From Figure 2, both spectra contain absorptions for  $\nu_{\text{NO}_2}$  at about 1514, 1336 cm<sup>-1</sup> for N=N at 1396 cm<sup>-1</sup> and for aryl at 1604 cm<sup>-1</sup>. The most noticeable difference is the lack of absorption at ~3440 cm<sup>-1</sup> for the OH stretching mode in the ART FT-IR spectrum, which not only indicates that both of the two hydroxy groups in NHPA molecules reacted with the Si(111) surface to form Si–O bonds but also rules out the possibility of the presence of NHPA in a physisorbed state. In our IR spectrum, because NHPA molecules contain azobenzene and C–O groups and because the corresponding peaks of phenyl–N and C–O bonds appear at 1144 cm<sup>-1</sup> and 1105 cm<sup>-1</sup>, respectively, which is the same region as Si–O–C peaks, we deduce that the asymmetric Si–O–C stretching vibration must have been combined into the peaks of phenyl–N and C–O bonds. To validate the chemical stability of NHPA-modified Si(111) surface, additional tests were performed according to the method previously reported.<sup>22,25</sup> The result showed that no distinct changes in the IR spectra were observed after 3 days exposure of the film to laboratory ambient.

Contact angle measurements and AFM were employed to research the changes of surface properties after UV and visible

light irradiation. The water contact angle measurements demonstrated that a reversible change can be observed. Irradiation with UV light for 30 s and the photochemical change from trans to cis form caused a change in wettability reflected in a water contact angle change from 78 to 83°, which is completely reversed by 30 s irradiation with visible light. This kind of cycle can be performed repeatedly. In the case of AFM studies, a mask with apertures in micrometer size regime was used as the imaging object. The mask was removed, and the topography of the modified Si(111) surface after irradiation was investigated by AFM. After 30 s irradiation with UV light, the isomerization from trans to cis form in the illuminated areas took place. Figure 3A shows the topographical image of a mask-patterned region. Regular arranged apertures could be observed clearly. Accordingly, the height of the molecules decreased by about 0.6 nm (see cross section in Figure 3B); this value well matches the length disparity of trans and cis isomer (Scheme 2). The cis form surface can reverse to a trans form after 30 s irradiation with visible light (Figure 3C), showing revisable characteristic.

The understanding of molecular electronic characteristic is extremely important in the development of molecular electronics. It is known that the molecular conductive characteristic depends on the structure of the molecules.<sup>34,35</sup> In our present study, the electric properties of Si(111) surface modified by NHPA molecules were assessed by probing the Si(111) surfaces using STM. The *I*–*V* curves, measured in air, were rather stable. During *I*–*V* measurements, the same tip was used, and the samples were under dark conditions to avoid the effect of illumination on NHPA molecule isomerization. For more accuracy, the typical *I*–*V* curves were attained in a statistic manner. From our experimental results, we found that the tunneling conditions had little influence on the conductive characteristic. At a set bias  $V_{\text{bias}} = 0.15$  V condition, the modified surface presented consistent results with changing tunneling currents from 0.03 to 0.1 nA. Figure 4 shows the *I*–*V* characteristics of the surface modified with NHPA molecules. The surface shows a drastic different conductive characteristic when NHPA molecules on it are in a different molecular conformation. First, the surface was irradiated for 30 s under





**Figure 4.** Typical  $I$ - $V$  characteristics obtained by applying a changeable voltage on (A) trans form and (B) cis form of NHPA monolayer on high-conductivity Si(111) surface. An electrochemical-etched tungsten tip was used. The curves shown are averages from five different experimental locations on the surface. Tunneling conditions:  $V_{\text{bias}} = 0.15$  V,  $I_t = 0.05$  nA. Scan rate: 1000 V/s.

visible light to ensure azobenzene molecules in trans form. The typical  $I$ - $V$  curve of such a surface shows a higher current in a low voltage range (Figure 4A). In contrast to the  $I$ - $V$  curve in Figure 4A, after 30 s UV irradiation, the tunneling current switched to a lower current at the same voltage conditions because of the trans-to-cis isomerization (Figure 4B). With alternate irradiation of the surface with UV and visible light, the conductance of the azobenzene-modified Si(111) surface exhibits a switching trait. In 10 cycles, the conductive characteristic of two kinds of isomers shows well reproducibility. On the basis of the photoinduced conformational change of NHPA molecules, the electric characteristic of the modified Si(111) surface can thus be well controlled. Trans and cis structural azobenzene molecules modified Si(111) surfaces show a difference in conductive characteristic, which is likely to be the result of the fact that a trans isomer has a more favorable conjugate plane than a cis isomer.

#### 4. Conclusions

In conclusion, photocontrolled surfaces have been successfully prepared by modifying the Si(111) surfaces with photoactive azobenzene-containing molecules (NHPA) via the formation of Si-O bonds. The resulting monolayer was very stable at ambient conditions. Trans/cis conformational transformation can be achieved by alternate UV and visible light irradiation. The surface modified with two different isomers exhibited a distinctive change in the conductive characteristic under STM measurements. Thus, the photoregulation of the electrical conductivity of Si(111) surface can be realized on the basis of the photoisomerization effect of azobenzene molecules. A similar modifying procedure on Si(111) surface is likely to be extended to other organic functional molecules. The potential applications of such functional hybrid surfaces in microelectronics and molecular electronics can be expected. The subtle structures and quantitative analysis of the modified surfaces are worth being further studied.

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**Supporting Information Available:** High-resolution XPS spectrum and fit of the Si 2p region and XPS spectra for a 90°

takeoff detection angle of the NHPA modified Si(111) surface. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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