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Photo Switchable Polysiloxane Self-Assembled Monolayer

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An azobenzene-spaced polysiloxane polymer was synthesized and characterized, and its isomerization was studied in solution and as a thin film by UV-Vis spectroscopy. The self-assembled monolayers (SAMs) on the silicon surface permit reversible molecular photoswitching. Contact angle results showed the hydrophilic nature of the trans-isomer compared to the cis-isomer. This was supported by the dipole moment calculation from density functional theory (DFT), which showed a higher value for the trans-isomer, thereby confirming its hydrophilic nature. The AFM study revealed polymeric brush-like structure on the silicon surface and confirmed its isomerization upon exposure to UV-Vis light.

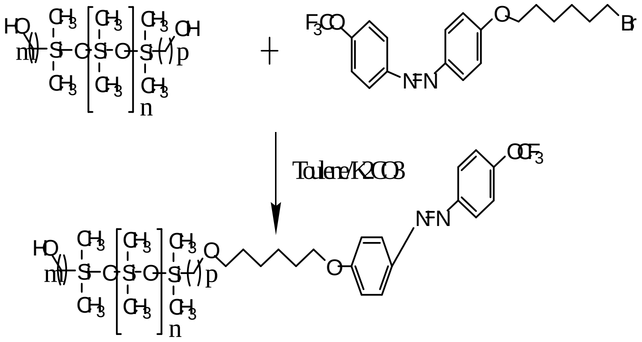
Keywords: Self-assembled monolayer; Photowettabality; Contact angle; Atomic force microscopy; Photo-isomerization

I. INTRODUCTION

Azobenzene-containing polymers (azopolymers) have gained more interest because of their potential use in various industrial science applications, example holographic recording, photomechanics, diffractive optics, and micro- and nanopatterning [1-7]. These applications exploit the efficient and photoswitchable isomerization of the azobenzene moieties between the trans-state and cis-state as a result of various changes in the properties of the material system both at the molecular and macroscopic levels .[7,8] Attractive properties have been reported for azo-containing siloxane polymers and co-polymers. For example, the azo content of side-chain siloxane copolymers and terpolymers was found to influence their phase behavior [9] and optodielectric switching [10].

The role of the siloxane spacer in side-chain azobenzene liquid-crystalline (LC) polymers was studied in applications in holographic grating[11,12] and the dipolar alignment of nonlinear optical (NLO) materials.[13,15] In this paper we describe a new polymer designed such that it contains a polysiloxane unit bound to an azobenzene unit with a trifluoromethoxy group. With the advent of molecular photo-electronic devices for future applications in microelectronics and bioelectronics, [16,17] progress in the development of functionalized and powerful organic monolayers that can be directly grafted onto silicon substrates has become important. The covalent bonding between the silicon substrate and the organic molecules improves their resistance, even under harsh conditions.[18,20] This constitutes a key advantage of self-assembled monolayers (SAMs) with organic thiols on gold surfaces whose stability seems less effective and subordinate to several factors[19,20]. For these reasons, the direct covalent grafting of polysiloxane containing an azobenzene group onto a hydroxilated silicon surface is reported.

However, to date, important issues, such as the ability of a polysiloxane unit to which an azobenzene unit containing a trifluoromethoxy group is attached to constrain trans/cis isomerization of the azobenzene unit with covalently grafted SAMs on the silicon surface, have not yet been studied completely for photo-driven molecular switching devices. This prompted us to report the characteristic photoresponsive behavior derived from the dynamic nature of the cross-linkers together with the ability of the newly designed anchored polymer to drive the self-assembly process. Polysiloxanes are highly twisting mobile polymers, which exhibit low glass transition temperatures, because of the chemical incompatibility resulting from the upright position of the siloxane backbone beneath the layer of chemisorbed hydroxyl alkyl chain attached to the Si surface; thus, the trifluoromethoxyazobenzene chains remain in a separate layer above the layer containing the siloxane backbone. In this work, a polymer backbone designed to obtain stable photosensitive flexible systems was used to synthesize the novel polysiloxane-spaced trifluoromethoxyazobenzene 1 (Scheme 1), following which the resulting reversibly photoswitchable SAMs on a silicon surface were characterized. We demonstrate the ability of this new type of polymer incorporating azobenzene to create highly stable long-lived trans-azobenzene by driving the self-assembly process. Upon illumination with UV light, the trans-azobenzene is converted to cis-azobenzene, whereas subsequent illumination with blue light switches the compound back to its trans-state, as indicated by their photowettability properties and density functional theory (DFT) calculations, which are in good agreement. The AFM study revealed the switching of the trans-cis isomerization by morphology change as indicated by the RMS roughness and peak heights of the two isomers. This makes photochromic siloxane-spaced azobenzene molecules more interesting for use in optical and optoelectronic materials.



Scheme 1. Synthesis of the polysiloxane bound photo switchable trifluoromethoxyazobenzene

II. MATERIALS AND METHODS

A. *Materials*

The polysiloxane-spaced trifluoromethoxyazobenzene was synthesized using α,ω-bis(hydroxyalkyl)-ended poly(dimethylsiloxane) (PDMS) (Mn=5600 g/mol) with (*Z*)-2-(4-(6-bromohexyloxy)phenyl)-1-(4-(trifluoromethoxy)phenyl)diazene[21] in toluene (1 : 1 w/v ratio of polymer with reactant) at 80 ^{o}C under reflux. The reaction was monitored by GPC analysis. The polysiloxane-spaced trifluoromethoxyazobenzene was characterized by FTIR, ^{1}H NMR, and ^{13}C NMR GPC. Copolymers incorporating PDMS represent a special category, owing to their remarkable properties. [22-24] Here we have successfully demonstrated the synthesis of polysiloxane-spaced trifluoromethoxyazobenzene under mild reaction conditions. We believe that the polymer may have a variety of industrial applications. Additional details of the preparation and characterization of the azobenzene-containing polysiloxane compound are provided as supporting information.

B. *Sample Preparation*

The formation of well-characterized, hydroxylated silicon oxide substrates was obtained by the following procedures. Si (111) wafers were cut into 1 × 1 cm^2 pieces and ultrasonicated in methanol and acetone to clean and degrease them. The cleaned Si wafers were treated with piranha solution by exactly following the literature strategy[25]. The substrates were cleaned with deionized water and dried in a stream of N_2 gas for several minutes. The –hydroxyl-terminated silicon surface was then exposed to a solution of compound 1 in anhydrous toluene (0.15 mM) for a period of 4 to 5 h, in a glove box and under an inert atmosphere (Figure 1.).

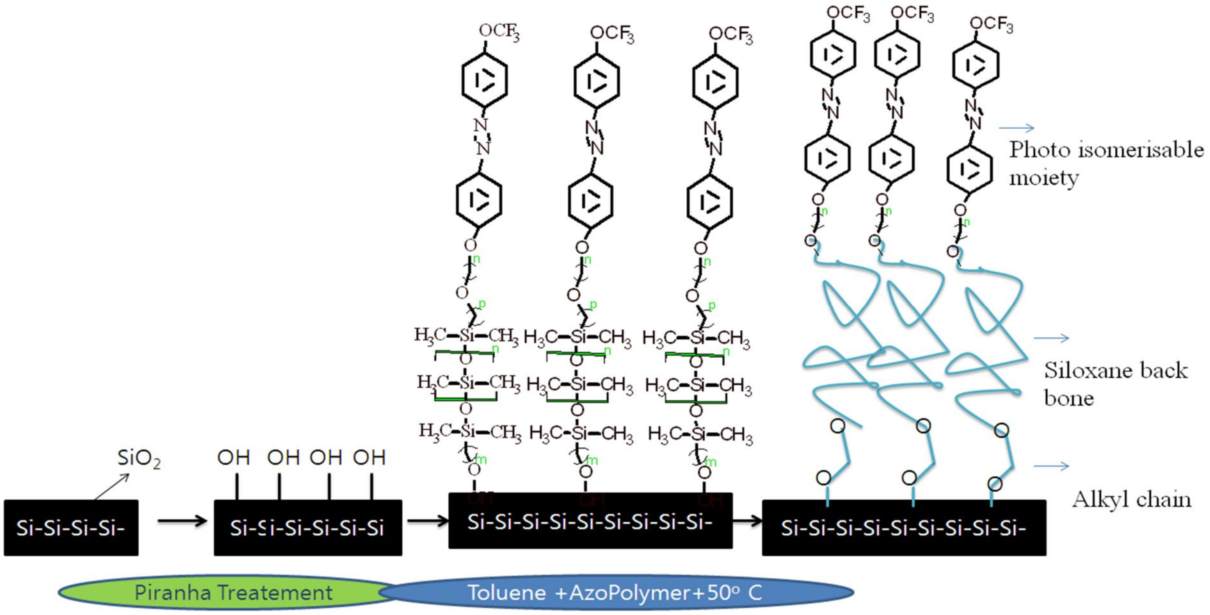


Figure 1. Self-assembled monolayer formation of polysiloxane-spaced azobenzene molecules on a silicon surface.

C. Characterization Techniques.

The contact angle was measured with a DSA100 contact angle system (Data Physics, KRUSS) at room temperature by using a 5-µL drop of water for the static contact angle ($ɵ_s$). X-ray photoelectron spectroscopy (XPS) data were measured with a Quantera SXM (ULVAC-PHI) electron spectrometer. Attenuated total internal reflectance (ATR) Fourier transform infrared (FT-IR) spectra were obtained on a 5900 and Continuum (Thermo) spectrometer in multiple internal reflection mode. Atomic force microscopy (AFM) characterization was done with an L-trace 11 multimode scanning probe microscope (Nano Fine Tech Co). The theoretical DFT calculations were done by using the DMol^3 program in the Materials Studio 4.2 package [26, 27]; that is, the quantum mechanical code was obtained using density functional theory. The Perdew-Burke-Ernzerh function of the Generalized Gradient exchange correlation function level [28] with a double numeric polarization basis set was used to obtain the energy level of the frontier molecular orbitals.

III. RESULTS AND DISCUSSION

A. UV-Visible Absorption Spectra

Figure 2. shows the change in the UV-Vis absorption spectra of compound 1 in toluene and as a thin film. The absorption maxima near 352 nm with a weak band at 437 nm correspond to the π–π* and n–π* transition bands of the *trans*-azobenzene, respectively.

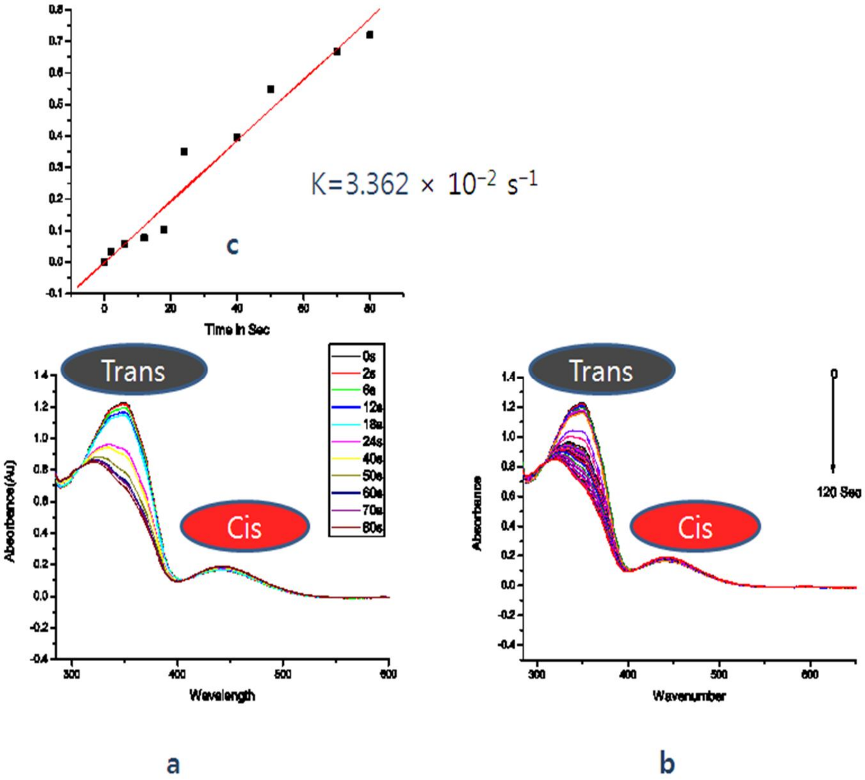


Figure 2. UV-Vis absorption spectra of polysiloxane-spaced azobenzene molecules in (a) toluene (0.08 w %) and (b) thin film on UV irradiation, and (c) shows the first-order plot for the *trans*–*cis* photo-isomerization.

Figure. 2(a) shows the changes in the UV absorbance of the polysiloxane-spaced azobenzene irradiated by UV at different time intervals, namely 0, 2, 6, 12, 18, 24, 40, 50, 60, 70, and 80 seconds, respectively. Clearly, an intense absorption peak located at 352 nm and a weak peak at about 437 nm indicate the π-π* electronic transition of the *trans*-azobenzene side chain and weak n-π* electronic transition of the *cis*-isomer, respectively. The kinetic constant of the photo-isomerization was calculated by using the intensity of the UV absorption at different irradiation intervals by formula (1).

$\ln (A_\infty - A_t)/ (A_\infty - A_0) = - K_{t\text{-}c} \longrightarrow (1)$

The slope of the curve formed by $\ln[(A_\infty - A_t)/(A_\infty - A_0)]$ as a function of time was denoted as the kinetic constant of the polysiloxane-azobenzene photo-isomerization and the value of $K_{t\text{-}c}$ obtained in this way was K=3.362 × 10^{-2} s^{-1}. This means the polysiloxane-azobenzene compound has unique properties.

B. Fourier Transform Infrared (FTIR-ATR)

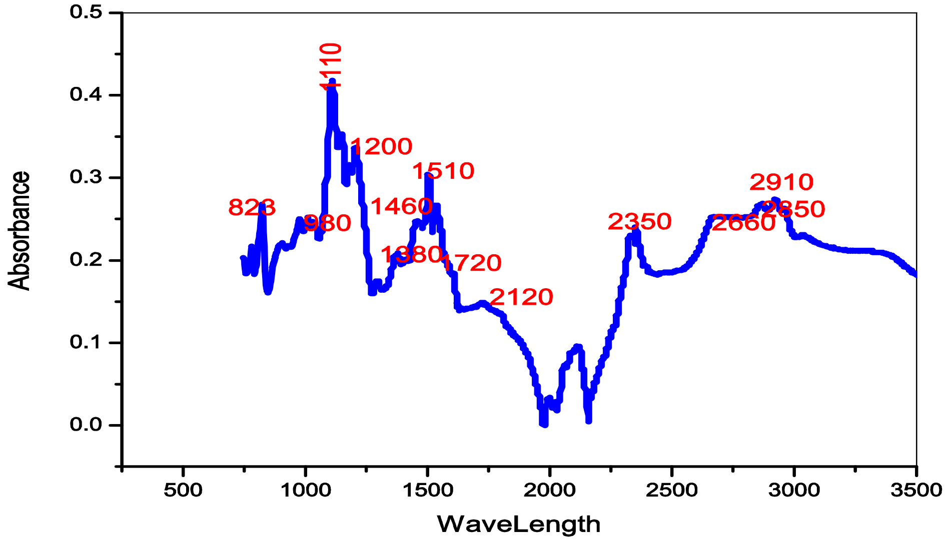


Figure 3. ATR FT-IR spectrum of Si (111) surface after grafting.

In Figure 3, the spectral result containing absorptions for N=N at 1380 cm^{-1} and for aryl at 1720 cm^{-1} are compared. The most distinguishable difference is the lack of absorption at 3440 cm^{-1} for the OH stretching mode in the ATR- FTIR spectrum, which indicates the absence of polysiloxane-azobenzene in the physisorbed state. The IR spectrum displays the bands of the azobenzene and C-O groups of the polysiloxane-azobenzene molecules: the corresponding bands of the phenyl-N and C-O bonds appear at 1200 cm^{-1} and 1110 cm^{-1}, respectively. As this is the same region in which the Si-O-C peaks appear, we obtain that the asymmetric Si-O-C stretching vibration must have been combined with the bands of the phenyl-N and C-O bonds. The bands of the asymmetrical and symmetrical (CH_2) appeared at 2910 cm^{-1} and 2850 cm^{-1}, respectively. This result indicates that no changes in the IR spectra were observed after three days of exposure of the film to ambient laboratory conditions.

C. X-ray Photoelectron Spectroscopy

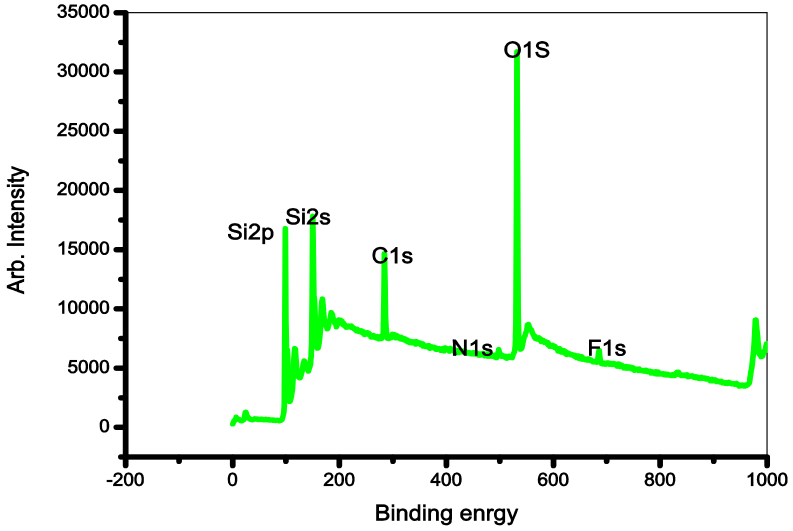


Figure 4. XPS spectra of the polysiloxane-spaced azobenzene monolayer on Si (111).

Figure 4. shows the XPS spectrum of the covalently grafted Si surface. Including the bands owing to the Si-substrate, the spectrum

exhibits peaks at N1s (402.4 eV) and C1s (285.8 eV). Additionally, there are two peaks at 535.7 and 679.4 eV, corresponding to O1s and F1s, respectively. The high-resolution XPS spectrum of the Si2p shows, in addition to the Si-substrate signal at 94.2 eV, a broad peak located at 148.8 eV in binding energy indicating the Si2s. This peak might also include suboxides, though the wide Si2p shoulder band at higher 103.0 eV, indicative of SiO_2, is absent.

D. Water Contact Angle

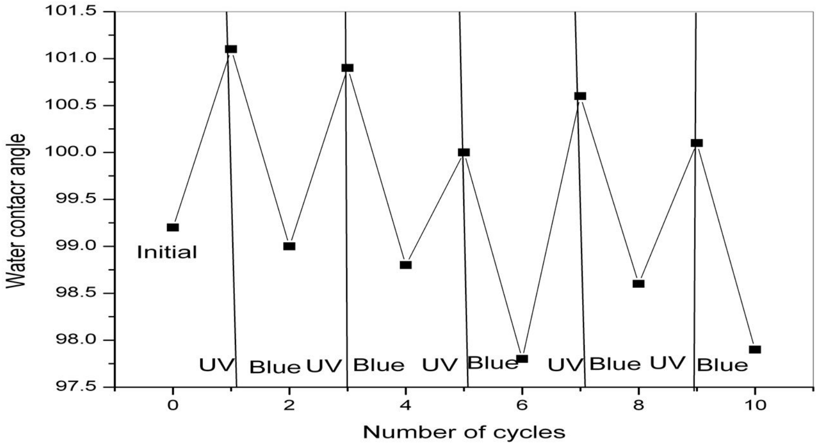


Figure 5. Evolution of water contact angle of the polysiloxane-azobenzene monolayer. The columns labeled trans and cis refer to the sample after irradiation with UV (360 nm) and He-Ar blue laser (465 nm) light.

High-intensity UV and visible light can therefore be used to obtain either the trans or cis form; hence, the light can be used to achieve photoswitching. The surface wettability was measured by contact angle goniometer, indicating that after UV and blue light irradiation the hydrophobicity of the trans-state is a little higher than that of the cis-state[29]. Thus, the contact angle of the trans-monolayer is expected to increase, whereas that of the cis-monolayer is expected to decease because of its larger dipole moment and weaker hydrophobicity. [30] Under irradiation with UV light (365 nm) for 20 min, the photochemical change from the trans- to the cis-isomer caused a change in wettability reflected in the water contact angle (y) from 99.2 to 101.1 in the first cycle, whereas it is completely reversed to the original value by 20 min irradiation with blue light (430 nm). Additional cycles continued to induce the photochemical change from trans to cis, as reflected in the water contact angle difference of 3^o (Figure 5.). This kind of cycling can be performed repeatedly. In our DFT calculation of the dipole moment of our molecule 1, the trans-isomer was found to be more hydrophilic compared to the cis-isomer, which is in agreement with the obtained contact angle result. This may be due to the bonding of the surface water molecules with the azo moiety during self-assembly, as illustrated in Figure. 6.

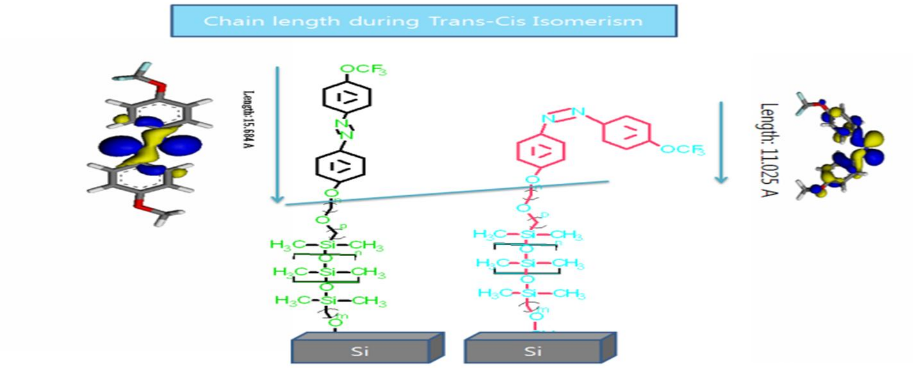


Figure 6. Molecular structure of photo-responsive Si (111) surface prepared by attaching amphiphilic polysiloxane-azobenzene molecules.

To probe this hypothesis further, we carried out first-principle calculations, in which the length of the molecule was found to be

15.684 Å for the trans-isomer and 11.025 Å for the cis-isomer, as shown in Figure 7. The calculated dipole moment of the trans- and cis-states of the molecule were found to be 4.6451 and 3.774 Debye, respectively.

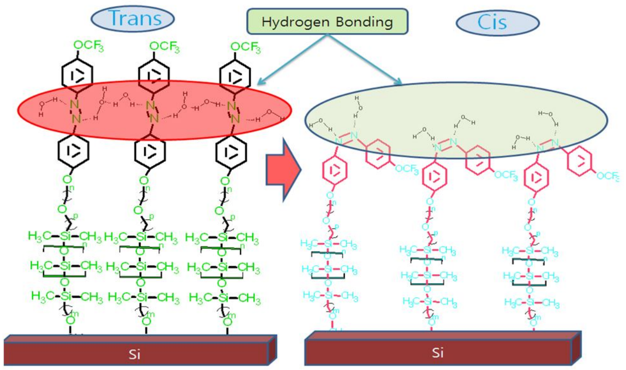


Figure 7. Proposed hypothesis for hydrophilic trans-cis isomerization with formation of weak hydrogen bonding between water present on the Si (111) surface and the -N=N- group of the polysiloxane-azobenzene monolayer.

E. *Atomic Force Microscope*

AFM studies were conducted to investigate the topography of the modified Si (111) surface after irradiation. When a freshly prepared monolayer was irradiated with 365 nm light, the brush-like structure disappeared and the surface became smooth and flat (Figure. 8). Therefore, the surface roughness value was significantly reduced from 6.732 × 10^{-1} nm to 5.568 × 10^{-1} nm owing to sufficient photo-conversion of the elongated *trans*-form to the bent *cis*-form. After 10 min irradiation with visible light of 436 nm, the brush-like structure partially reappeared, thereby indicating the occurrence of isomerization from the *cis*- to the *trans*-form in the penetrated areas.

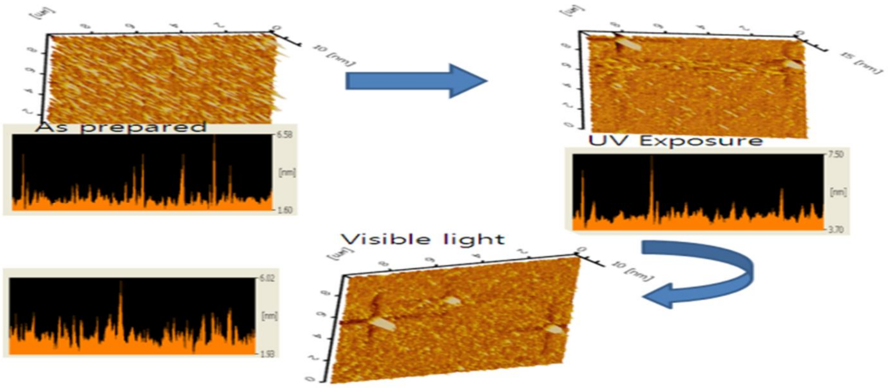


Figure 8. AFM topographic image of the prepared polysiloxane-azobenzene SAMs on a Si (111) surface. The characteristic brush-like structure disappeared and the surface became smooth after irradiation with 365 nm light for 10 min. The brush-like structure partially recovers upon irradiation with visible light for 10 min.

Accordingly, the height of the molecules varied (see cross section in Fig. 8); this difference corresponds well with the length disparity of the *trans*- and *cis*-isomer. The *cis*-form switches to the trans-form after 20 min irradiation with visible light, clearly demonstrating the photoswitching characteristic. An understanding of the molecular electronic behavior is extremely helpful in the development of applications based on molecular electronics.

IV. CONCLUSION

In conclusion, photocontrolled surfaces were successfully prepared by modifying the Si (111) surfaces with photoactive azobenzene-containing molecules (polysiloxane-azobenzene). The self-assembled monolayer that was obtained was very stable under ambient laboratory conditions. *Trans*/*cis* photoswitching could be achieved by alternating the UV and visible light irradiation. The surface modified with two different isomers exhibited a distinctive change in the AFM study, indicating a change in the RMS roughness and peak heights of the formed brush-like surface. Thus, the photoregulation of the Si (111) surface can be realized by the photo-isomerization effect of the azobenzene molecules. Organic functional hybrid surfaces of this nature are expected to find application in microelectronics and molecular electronics. Subtleties in the structures and a quantitative analysis of the modified surfaces, including the mechanistic changes in the surface morphology, are worthy of further study.

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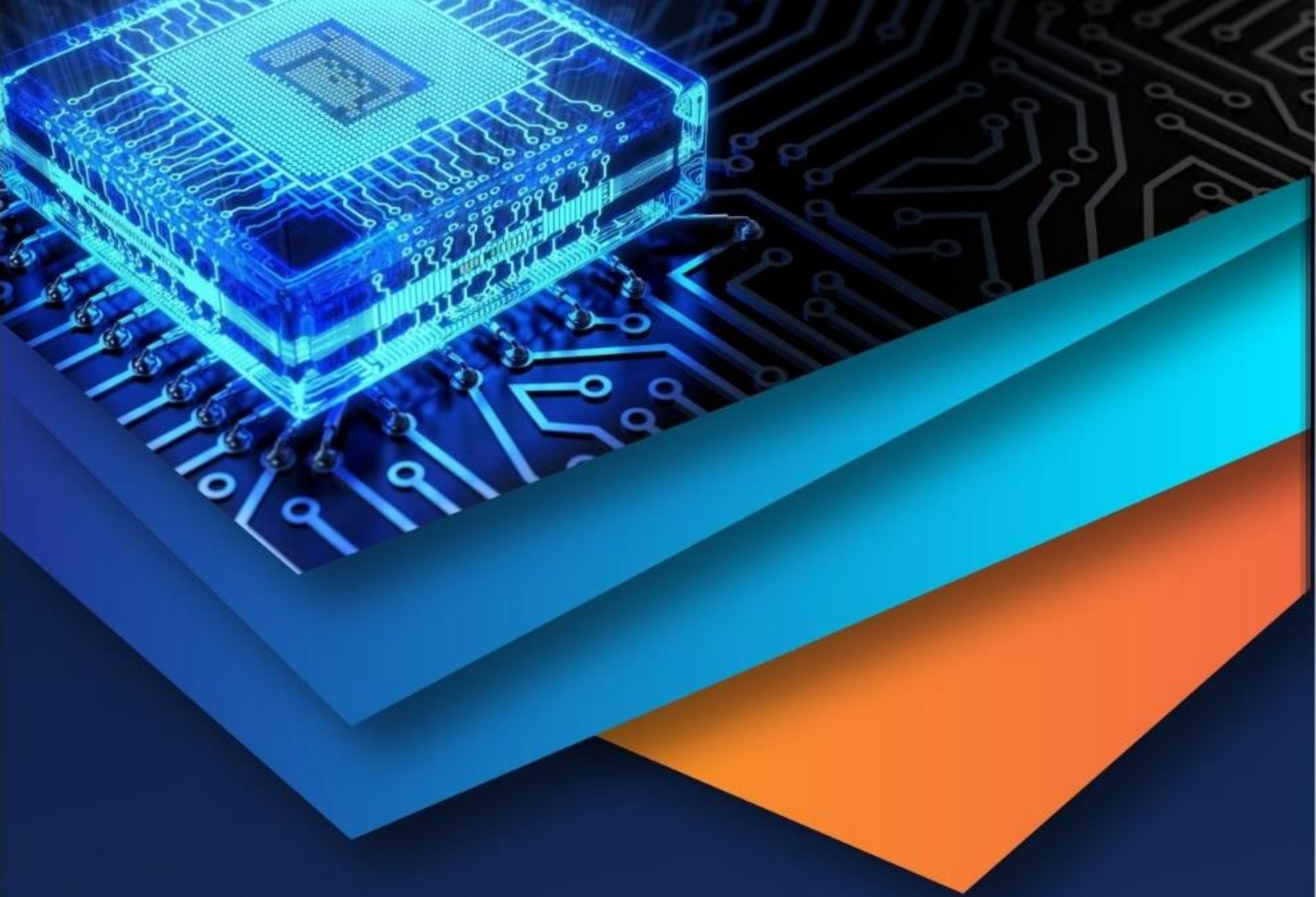

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