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Molecular Grafting to Silicon Surfaces in Air Using Organic Triazenes as Stable Diazonium Sources and HF as a Constant Hydride-Passivation Source

Bo Chen, Austen K. Flatt, Huahua Jian, Jared L. Hudson, and James M. Tour*

Department of Chemistry, Department of Mechanical Engineering and Materials Science, and Center for Nanoscale Science and Technology, Rice University, MS-222, 6100 Main Street, Houston, Texas 77005

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Aryl molecules were covalently grafted to hydride-passivated Si(100) surfaces (Si−H) by the in situ conversion of aryldiethyltriazenes into aryldiazonium salts using 2% HF, followed by spontaneous surface grafting of the aryl species to the silicon surface. Major advances are as follows: first, reactive diazonium species need not be isolated, and second, by using aqueous HF as the triazene-to-diazonium conversion promoter, the entire process can be carried out in air since any Si-oxide is continuously converted to the Si−H species. Molecular layers from a monolayer to 200 nm thick could be formed depending on the reaction conditions used. In one case where the molecule bore an α-triazene and ω-aniline (**6**), after grafting of the molecular layer onto Si−H via the triazene, the remaining aniline moiety was converted into a diazonium salt in situ with NOBF$_4$ and then permitted to react with functionalized single-walled carbon nanotubes (SWNTs), thereby covalently attaching nanotubes to the silicon surface using the aryl molecular layer as a tethering unit.

Introduction

As the semiconductor industry approaches the limit of complementary metal-oxide semiconductor (CMOS) technology, efforts are underway to develop strategies to extend the life of silicon technology.[1] These processes could involve building functional structures atop semiconductors by relying on the spontaneous self-assembly and self-patterning of organic molecules at the surface of the substrate. In our work on NanoCell molecular memories,[2] we found that formation of metallic nanofilaments via electromigration was the source of the observed switching effect. It is often difficult to avoid metallic nanofilament formation; hence, the recording of molecular behaviors in metallic junctions can be complicated.[3] The direct covalent grafting of aryl molecules onto hydride passivated silicon surfaces via the reaction of aryldiazonium salts[4] creates an opportunity for developing molecular electronic devices that do not have metal electrodes in direct contact with molecular species, thereby obviating the formation of metallic filaments and providing a venue for recording of molecular electronic behavior. Furthermore, covalently bound conjugated molecules may serve as surface dopants to silicon that could play an important role in doping ultrashallow channels. We describe here a method to covalently graft organic arenes to hydride-passivated Si(100) surfaces (Si−H) by the in situ conversion of aryldiethyltriazenes, **1**−**5**,[5] and **6**[6] (Figure 1), into diazonium salts using dilute aqueous HF. Reactive diazonium species need not be isolated, and with use of aqueous HF in the reaction medium, the entire process can be carried out in air since any Si-oxide is continuously converted to the Si−H species. Therefore, the process is compatible with simple organic device fabrication methods and paves the way for diverse silicon-molecule studies in, for example, molecular electronics, sensors, and photo-electrochemical-based conversion arrays.

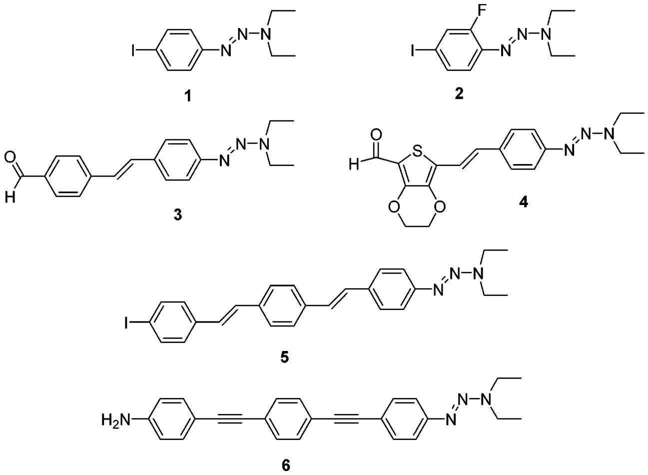

Figure 1. Triazenes **1**−**6** used in the present study.

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* To whom correspondence should be addressed. E-mail: tour@rice.edu.

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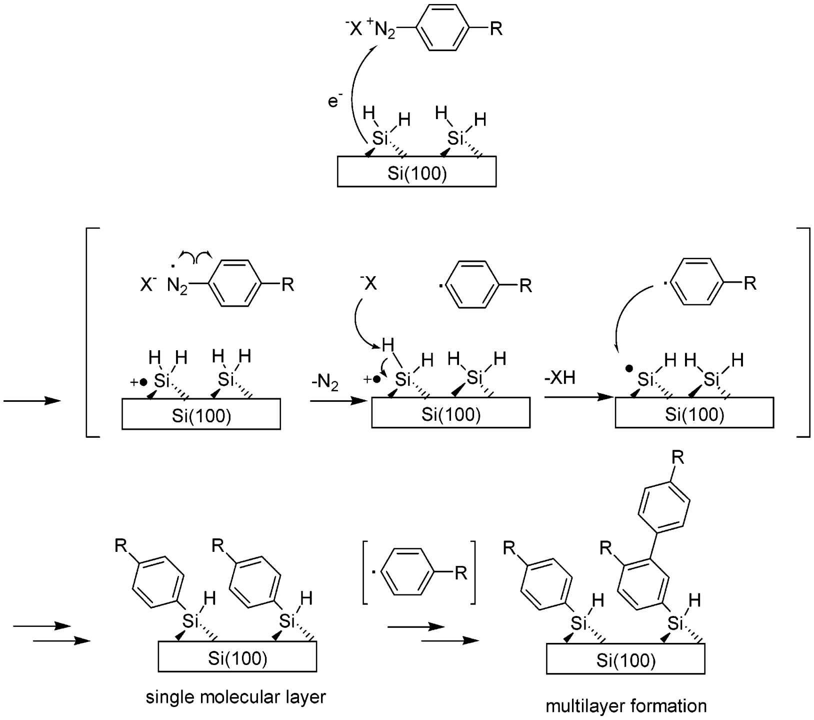
Scheme 1. Proposed Mechanism for the Reaction of Aryldiazonium Salts with Si(100) Surface[4] [a]



[a] Monolayer formation is achievable; however, multilayer formation can be facilitated through higher reaction concentrations and prolonged reaction times (hours).

In a related area, one of the potential applications of single-walled carbon nanotubes (SWNTs) is as electrodes in the next generation of electronic and testing devices.[7] To realize this goal, the SWNTs must be accessible for assembly, and attachment to silicon could provide a desirable interface for many molecular electronic arrays. SWNTs are known to react with aryldiazonium salts,[8] producing SWNTs functionalized by aromatic moieties upon loss of N_2. Dovetailing with the methods here, we show that the aryltriazene **6** grafting to Si−H can be used in sequence with a selective aniline-to-diazonium conversion for the bridging of SWNTs to silicon surfaces via the molecular layer.[6]

Experimental Section

Si(100) shards (prime grade, As-doped) were cleaned in piranha solution (2:1 H_2SO_4:H_2O_2) at 100 °C for 30 min and then rinsed with pure water (resistivity > 18 MΩ cm^{-1}). The shards were immersed in etching solution, a mixture of 4% aqueous HF and CH_3CN (v:v, 1:1; hence 2% HF overall) for 5 min under an Ar atmosphere. Organic triazenes **1**−**5** were dissolved in 10 mL of CH_3CN at various concentrations before being added to the etching solution containing the Si(100) wafer. The reaction vessel was sealed with a fitted lid and the container was agitated on a platform shaker at 100 rpm. After the reaction, the substrates were rinsed with copious amounts of deionized H_2O and CH_3CN and then dried with a stream of N_2.

The film thickness was measured using a single wavelength (632.8 nm laser) Gaertner Stokes ellipsometer. The n and k values were taken for each substrate. The thickness was modeled as a single absorbing layer on the top of an infinitely thick substrate (fixed n_s). A Quantera X-ray photoelectron spectroscopy (XPS) scanning microprobe was used in collecting the XPS data; the takeoff angle was 45°, and 114.8 W monochromatic Al X-ray source was applied for all the measurements. All XPS peaks were referenced to the C_{1s} major peak at 284.5 eV.

Functionalized SWNTs[8] were prepared by treating 600 mL of an SDS suspension of SWNTs (40 mg/L, 0.024 g, 2.0 mequiv of C) with 4-*tert*-butyldiazobenzene tetrafluoroborate (0.992 g, 4.0 mmol). The pH of the solution was adjusted to 10 with 6 M NaOH, at which point the mixture was allowed to stir for 3 h. After completion of the reaction, the mixture was diluted with acetone and filtered over a polycarbonate membrane (1 μm pore size). The filter cake was washed with water (100 mL) and acetone (200 mL) and then dried (30 mg). The TGA mass loss was 31.5%. The Raman D to G band ratio was 0.30.

Organic triazene **6**,[6] bearing the aniline group on one end and the triazene moiety on the other, was assembled on the hydride-passivated silicon surface using the same protocol as that used for compounds **1**−**5**. Following assembly, the silicon shard was immersed in a dilute solution of *tert*-butylphenyl-functionalized SWNTs in chloroform. An $NOBF_4$ solution (0.5 mM, 5 mL) in anhydrous acetonitrile was then added to the mixture containing the silicon shard. After 30 min, the sample was removed, rinsed with acetonitrile and chloroform, and dried using a stream of N_2. A Digital Instruments Nanoscope IIIa tapping mode instrument was used to obtain AFM images of the covalently attached SWNTs.

Results and Discussion

In the reaction of aryl diazonium salts with silicon hydride surfaces, radicals are believed to be the reactive intermediate, thus forming an organic molecular layer as shown in Scheme 1 for the Si(100) surface. The radical-based mechanism has been supported by previous studies in our laboratory.[4]

Some diazonium salts are not stable to oxygen; hence the reaction must be conducted in a glovebox, under a nitrogen

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Scheme 2. Assembly of the Functionalized SWNTs to the Film Derived from 6 on Si(100)

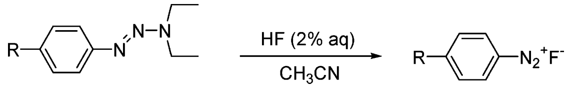


Table 1. Calculated Molecular Length for Triazenes 1−5

compound	calcd molecular length (nm)
1	0.7
2	0.7
3	1.4
4	1.3
5	2

Table 2. Film Thickness for in Situ Reaction of Triazenes 1−5 in 2% HF Solution on Si(100)

entry	compound	concentration (mM)	time (h)	measured film thickness (nm)[a]
1	**1**	0.2	0.5	4.0 ± 0.3
2	**1**	0.2	0.5[b]	1.7 ± 0.2
3	**1**	0.2	2	29.0 ± 1.2
4	**1**	0.2	2[b]	39.0 ± 1.5
5	**1**	20	0.5	149.0 ± 1.5
6	**1**	20	1	165.0 ± 1.8
7	**1**	20	2	156.0 ± 1.5
8	**2**	0.3	0.5	0.4 ± 0.2
9	**2**	0.3	2	5.3 ± 0.6
10	**2**	0.3	20	3.6 ± 0.4
11	**2**	20	1	195.0 ± 18.8
12	**2**	20	2	205.0 ± 20.0
13	**3**	0.2	0.5	4.9 ± 0.5
14	**3**	0.2	1	9.6 ± 0.6
15	**3**	0.2	1[b]	9.9 ± 0.5
16	**4**	0.2	0.5	7.3 ± 0.3
17	**4**	0.2	0.5[b]	6.9 ± 0.3
18	**4**	0.2	1	9.1 ± 0.4
19	**4**	0.2	2	9.7 ± 0.8
20	**4**	0.2	2[b]	8.1 ± 0.9
21	**5**	0.3	0.5	1.0 ± 0.2
22	**5**	0.3	1	1.2 ± 0.3
23	**5**	0.3	2	1.6 ± 0.3
24	**5**	0.3	16	3.2 ± 0.3

[a] The measured values are the average of three identically prepared samples. [b] Solid BHT was added to a final concentration of 0.01 M.

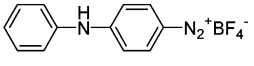
atmosphere. Furthermore, some diazonium species are not stable to isolation; therefore, their direct reaction with Si−H cannot be carried out. There are also potential safety hazards involved with the production and storage of some diazonium salts. The use of organic triazenes overcomes these limitations by offering an air-stable compound that can be converted in situ to the corresponding diazonium salt with the use of an appropriate acid,[9] as shown in Scheme 2. When the diazonium salt is generated by acid treatment in the presence of a hydride passivated silicon surface, a covalently bound organic layer is formed. This process was done under ambient conditions in air (vide infra). In some cases, butylated hydroxytoluene (BHT) was added in an attempt to retard multilayer formation. The calculated molecular lengths of triazenes **1**−**5** are shown in Table 1 and the film thicknesses generated, measured by ellipsometry, under different reaction conditions are listed in Table 2.

Table 3. Atomic Concentration and Film Thickness of 2 in the Presence and Absence of Air[a]

		atomic concentration				
entry	conditions	C_{1s}	O_{1s}	F_{1s}	I_{3d}	film thickness (nm)
1	air	73.9	16.4	9	0.7	195.0 ± 18.8
2	Ar	78.1	5.3	8.7	<0.1	25.0 ± 2.0

[a] Nitrogen comprises the remainder of the detected elements.

Five dilute acids, HF, HCl, HBF_4, AcOH, and trifluoroacetic acid (TFA), were surveyed to discover which acid generated the diazonium salts in highest yield. After a reaction time of 1 h, it was found that film formation only occurred in the HF solution. Apparently, the presence of HF was necessary to ensure a fresh hydrogen-terminated silicon surface in the presence of the water (from the acid) and atmospheric oxygen. When these conditions are used, dilute aqueous HF acts both as an acid for the triazene-to-diazonium conversion as well as an etching agent for the continuous silicon-oxide to Si−H conversion. By increasing the concentrations of the triazene solutions of **1** and **2** to 20 mM (Table 2, entries 5, 6 and 11, 12, respectively), we found that they formed multilayers up to 200 nm thick in 1 h. This could prove to be useful if seeking, for example, extended low κ dielectrics for electronic pattern layering on Si wafers. The addition of BHT to the triazene reaction mixture, to hinder radical processes, led to thinner films in some cases (Table 2, compare entry 1 to entry 2), while in several other cases there was little to no effect; the proposed radical mechanism may be too fast for interception of radical intermediates by the BHT at the surface.



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When diazonium salt **7**[10] was subjected to the assembly conditions described here (aqueous HF/CH_3CN in air), in the absence or presence of BHT, monolayer films were assembled on the Si(100) surface, with thickness of 1.4 and 1.3 nm, respectively. This result is identical to film assembly using the standard diazonium reaction procedure in a glovebox[4] and confirms that direct grafting of the film can take place in a mixture of HF and CH_3CN.

Brown precipitates were observed during film assembly of triazenes **1** and **2** at the 20 mM concentrations (but not at the lower concentrations) after 1 h. This could indicate that I_2 may have formed during the reaction with concomitant multilayer formation. This was further investigated using **2**, by repeating the reaction in air or under Ar for 1 h at 20 mM. After film formation the substrate was rinsed with water and acetonitrile and dried with nitrogen. The film thickness was measured and XPS data were collected for the films. The film thickness and the atomic concentration for C, O, F, and I from multiplex scans for the two samples are listed in Table 3.

When the reaction was performed in air (entry 1), the film thickness (∼195 nm) was much greater than when the film was assembled under Ar (∼25 nm, entry 2). By XPS the oxygen content of the film produced in air is about 3 times that of the film produced in Ar. The incorporation of oxygen into the film indicates that oxygen might have an important role in multilayer formation.

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(10) See Supporting Information for synthesis of **7**.

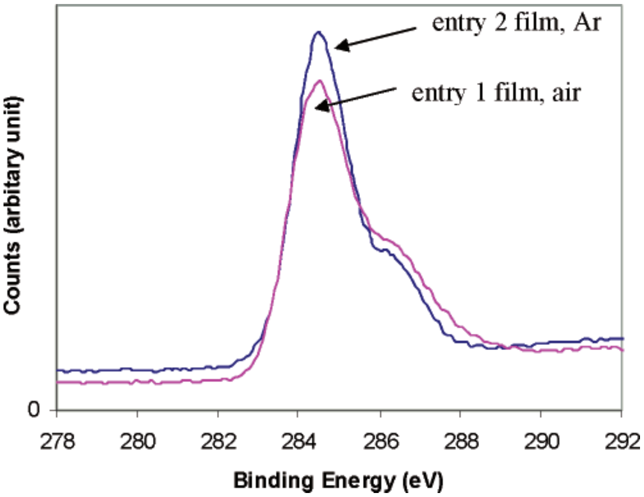
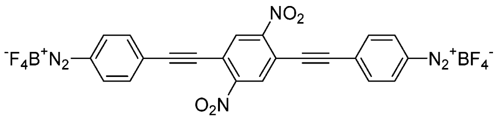


Figure 2. C_{1s} XPS spectrum of **2** from entry 1 and 2 films (Table 3) under air and argon atmosphere.

Figure 2 shows XPS C_{1s} core level spectra in the films from entries 1 and 2, Table 3. The main peak at 284.5 eV is attributed to the aryl carbons, and the subpeak at around 286.5 eV is the contribution from the $-C-O$ bond or the $-C{=}O$ bond. However, there is no detectable $C-F$ peak at 288 eV, indicating that no $C-F$ species are present in the film.[11] Based on the observation of the dark precipitate and the XPS data, both the iodo- and fluoro- groups were lost from the aryl rings during the assembly process. The F_{1s} signal remained even after sonicating the samples in water for a few minutes, indicating that F is trapped in the film. Since the loss of iodine and fluorine from the aromatic ring of **2** occurred both in the presence and absence of air, the mechanism by which oxygen is incorporated into the film may not be connected to the loss of the halides. Further work is ongoing to discern the details of this process.

Since the attachment of aryldiazonium salts to SWNTs is a known process,[6] we attempted the standard[4] assembly of the bis-aryldiazonium ion **8**[12] onto the silicon surface, hoping to retain the distal diazonium moiety after film assembly to provide a site for attachment of SWNTs atop the grafted molecular layer. However, after treatment of Si−H with **8** and washing of the grafted layer, the XPS signal corresponding to the N_{1s} spectra in $-N_2BF_4$, which occurs from 402 to 404 eV,[13] was not observed following film assembly. Based on the XPS results, both diazonium species are lost during assembly. After initial assembly on the Si surface, the conjugated molecule likely receives an electron from the Si, causing a reduction and subsequent loss of N_2 from the terminal site prior to analysis.



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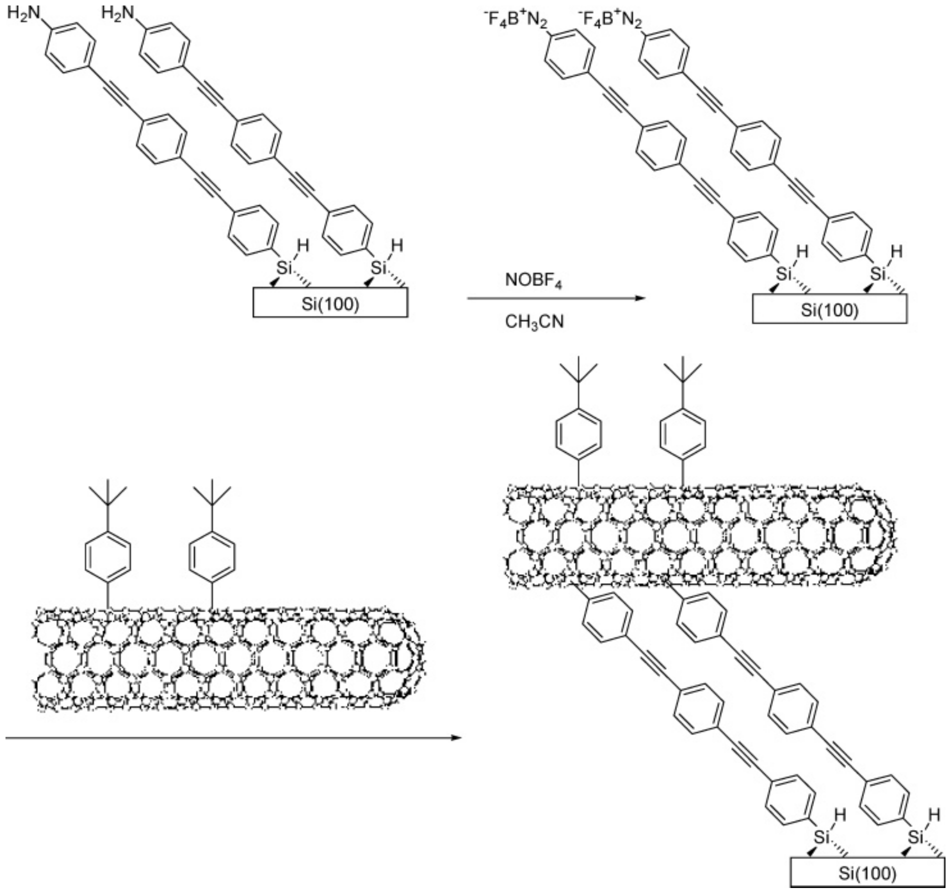
To attach SWNTs to silicon surfaces, we therefore explored the chemistry disclosed here. The aniline moiety that remained after grafting a layer derived from **6** to the silicon surface was further converted to a diazonium salt in situ using $NOBF_4$ in the presence of functionalized SWNTs

Scheme 3. Formation of Aryldiazonium Salts from Aryltriazenes



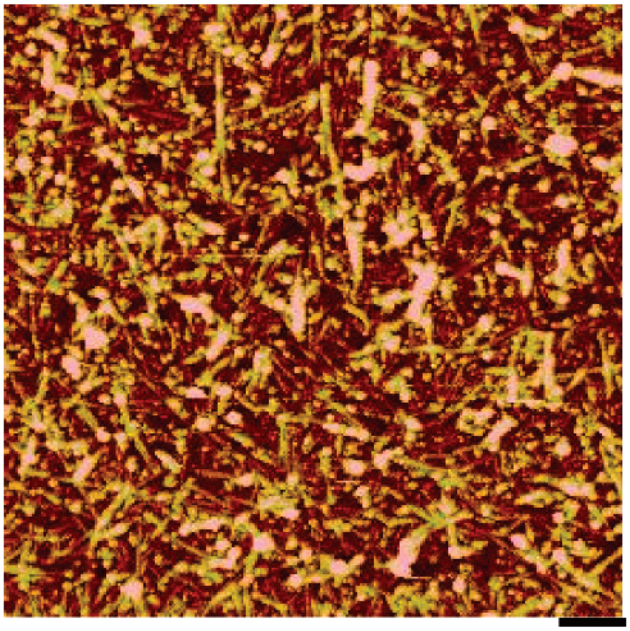


Figure 3. AFM image of SWNTs covalently bound to the organic thin film derived from **6** on the silicon surface. The height of the SWNTs ranges from 0.8 to 3.2 nm. Multiple measurements were made at 10 different locations to obtain the average height data. Black bar in lower right = 100 nm.

to produce the desired layer of SWNTs bound to the silicon surface via the intermediate layer of aryl molecules (Scheme 3). The diazonium-tipped surface-grafted molecules were stable enough to permit the in situ assembly to occur.

The AFM image of the SWNT-aryl-Si assembly formed from triazene **6** (Scheme 3) is shown in Figure 3. It can be seen that the substrate surface is well-covered with SWNTs.

Based on the height measurement in the AFM, it can be determined that the nanotubes are most likely individuals or small bundles with heights ranging from 0.8 to 3.2 nm. Since the silicon surface itself is not flat after the in situ film assembly process, with increases in roughness due to the layer of organic film and the fact that $NOBF_4$ slowly etches silicon surfaces (as shown by our control tests), some of the tubes may be extending out of the surface plane. In other cases, there may be molecules or other nanotubes underneath the SWNTs, yielding a higher apparent height. The surface-bound SWNTs were stable to rinsing and short sonication (30 s) under solvent. Control experiments were performed to ensure that the $NOBF_4$ diazotization step was required for SWNT attachment. Indeed, when the $NOBF_4$ diazotization step was eliminated, there was no attachment of the SWNTs to the silicon surface (Supporting Information). In previous studies for grafting SWNTs to Si, $NOBF_4$ could not be used since, in the presence of water, severe etching of the Si surface ensued.[6] However, anhydrous conditions ($CHCl_3-CH_3CN$) were utilized here. Therefore, the junctions prepared from silicon-molecule-SWNTs could prove to be excellent nonmetallic molecular electronic interfaces.

Conclusions

We have developed a convenient in situ film assembly using organic triazenes for the formation of Si-molecule assemblies under ambient conditions. Dilute aqueous HF serves as the reagent necessary for the organic conversion (triazene to diazonium) and concomitantly acts as an in situ etchant for Si−O to Si−H conversion, thereby making the reactions possible in air. Most of the triazenes formed thin films, with **1** and **2** forming layers 200 nm thick due to halogen loss. These latter films may be useful as low-*k* dielectrics. A direct covalent bond between a bulk contact surface and organic molecule allows stronger electric coupling, paving the way for further device investigations.[14] We successfully bound functionalized SWNTs to the monolayers derived from an aryldiazonium intermediate grafted onto a Si(100) surface, producing nonmetallic molecular junctions. Use of these Si-molecule-SWNT junctions for electronic device formation is currently being explored and the device behavior will be disclosed shortly.

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Supporting Information Available: Synthesis of **7** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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