Chemical Reactions in Monolayer Aromatic Films on Silicon Surfaces

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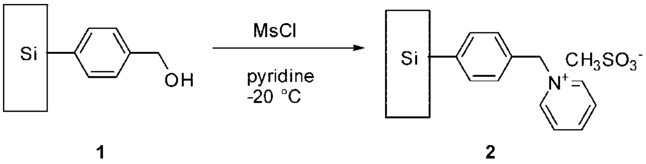
The formation of thin films on solid surfaces can be limited by the structures of the molecules and protocols used to form the films. These limitations can be mitigated by performing additional chemistry on the thin films to modify the structures and attach molecules with specific electronic, optical, or magnetic properties. In the present work, aryl molecules were covalently grafted onto hydride-passivated Si(111) surfaces (Si−H) to form monolayer films. The reaction of the films with selected reagents produced polar films and films containing fullerenes and organometallic compounds. Fullerene molecules were attached onto the surfaces via monolayer films in two ways: diazonium salt reaction with pristine fullerene and reaction with *N*-methylfullerenepyrrolidone. The films were characterized by X-ray photoelectron spectroscopy and ellipsometry. The reactions expand our capabilities to produce thin films on silicon with potential applications in molecular electronics, optical devices, and other related areas.

Introduction

Research on the grafting of molecules to surfaces such as silicon was carried out with the expectation that the technology could be used in the development of molecular electronic devices, chemical sensors, and other areas of interest.[1–5] The nonmetallic structured devices might open a door for the semiconductor industry to produce a new generation of memory devices.[6] However, in our hands, the choices of aromatic films that can be formed through direct grafting onto silicon surfaces are limited by the diazonium or triazene chemistry that is used; the protocol does not allow the attachment of molecules with certain structures and functional groups.[1,3] However, the desired properties of the thin films can be achieved by reaction between the films and molecules containing the structures or functionalities of interest. As an example, we have observed a higher current and larger hysteresis using modified thin films on a molecular electronic device.[7] Reactions to modify self-assembled monolayers (SAMs) of aliphatic monolayers on different substrates such as gold, glass, and indium−tin oxide surfaces have been reported, but less work on aromatic film reactions has been reported, especially for reactions with thin films on silicon surfaces.[8–17]

Scheme 1. Reaction of Film 1 To Form the Mesylate Salt 2



In the present work, it has been demonstrated that thin films, once formed on Si(111) surfaces, can be chemically modified. For instance, a benzyl alcohol film **1** grafted to a silicon surface[18,19] was quaternized with methanesulfonyl chloride (MsCl) and pyridine to form the highly polar film **2** (Scheme 1). It is expected that the polar film **2** will affect the electrical characteristics of the silicon to which it is attached.

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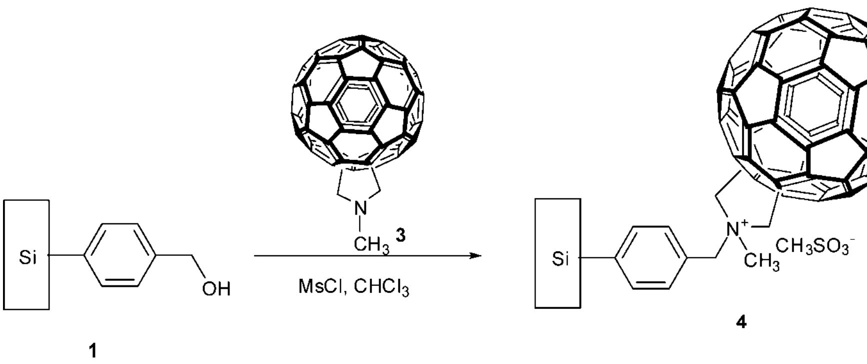
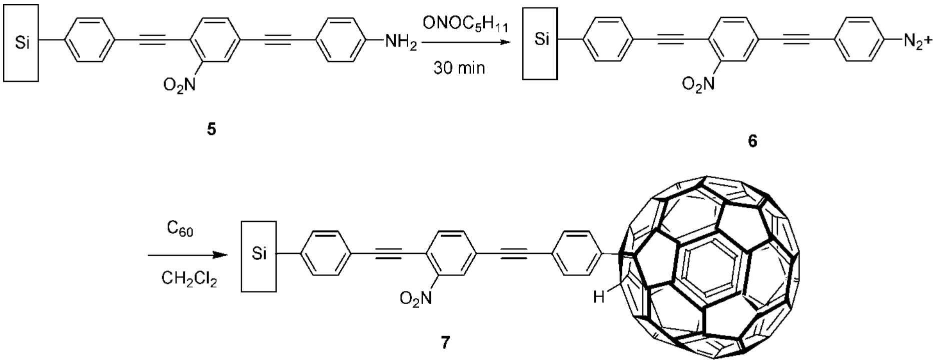
Scheme 2. Reaction of Film 1 with Functionalized C_{60} (3) To Give Film 4

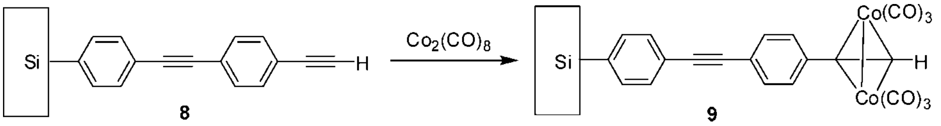


Scheme 3. Diazotization of Film 5 followed by the Coupling of the Reactive Film 6 with C_{60} To Produce Film 7[a]



[a] The second bonding group to the C_{60} is unknown. It is presumed that the other valence site is occupied by H, although we have no confirmation.

Scheme 4. Reaction of Film 8 with Octacarbonyldicobalt To Produce Film 9



Fullerenes have attracted intensive attention since the discovery of their extraordinary structure and potential applications in many areas.[20,21] Each fullerene molecule can hold multiple electrons and exhibit characteristic electrochemical and electronic properties.[22] However, fullerene reactions on surfaces usually proceed under conditions different from those reported for bulk reactions. In an effort to study the physical characteristics of fullerenes chemically bonded to films on surfaces, fullerenes were attached to the film through two procedures, one using *N*-methylfullerenepyrrolidone (**3**; Scheme 2) and the other using pristine fullerene (Scheme 3). The latter was based on the procedure developed to attach single-wall carbon nanotubes to films on surfaces.[2] In Scheme 2, film **1** was quaternized using MsCl and **3** in chloroform to produce film **4** containing fullerenes attached to the film on the silicon surface.

In Scheme 3, the aromatic film **5** with distal aniline functionality[2] was converted to the diazonium film **6** using isoamyl nitrite;[2] the film **6** was then exposed to fullerene in methylene chloride to produce the fullerene-containing film **7**.

Octacarbonyldicobalt is a relatively stable cobalt complex that has been widely used as a reagent in organic synthesis.[23,24] When reacted with alkynes, stable organometallic compounds are formed.[25,26] The ferromagnetic properties of cobalt could expand the applications of the modified thin films. The reaction between the acetylenic end group of film **8** and octacarbonyldicobalt (Scheme 4) to make film **9** was investigated.

Experimental Section

General Procedures. Unless noted otherwise, reactions were performed under a nitrogen atmosphere. Ethyl acetate and toluene were distilled from CaH_2. All other commercially available reagents were used as received unless noted otherwise. Reactions were magnetically stirred and monitored by thin-layer chromatography using E. Merck silica gel 60 F_{254} precoated plates (0.25 mm) unless stated otherwise. 4-(Hydroxymethyl)benzenediazonium tetrafluoroborate (**10**)[18] and **3**[19] were synthesized according to the literature

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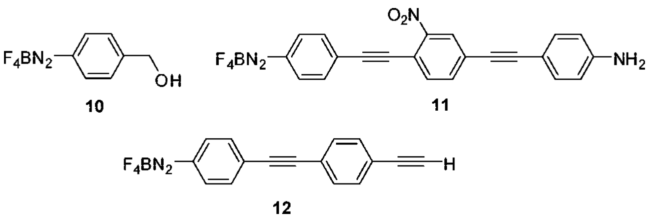
Table 1. Conditions for the Formation of Films 1, 5, and 8 on Si(111) in Anhydrous CH_3CN

diazonium salt	reaction time (h)	product film
10	0.5	**1**
11	1	**5**
12	0.5	**8**

procedures. The syntheses of **11** and **12** (Chart 1) were published elsewhere.[2]

Chart 1. Diazonium Salts 10−12 Synthesized Using Known Procedures



Ellipsometric Measurements. Measurements of surface optical constants and molecular layer thickness were taken with a single wavelength (632.8 nm) laser Gaertner Stokes ellipsometer. The n value for the hydrogen-passivated Si(111) surface was 3.83, and k was −0.02. The surface thickness was modeled as a single absorbing layer atop an infinitely thick substrate (fixed n_s). The observed error in repeated measurements of the same spot was typically less than 0.2 nm.

X-ray Photoelectron Spectroscopy (XPS) Measurements. A Quantera XPS scanning microprobe was used in collecting the XPS data. The takeoff angle was 45°, and a 114.8 W monochromatic aluminum X-ray source was used for all of the measurements. All XPS peaks were referenced to the C 1s major peak at 284.5 eV.

Film Assembly on Silicon Surfaces. Si(111) wafers (prime grade, arsenic-doped) of n-type were cleaned in a piranha solution (2:1 H_2SO_4/H_2O_2) followed by rinsing copiously with water (resistivity >18 MΩ cm^{-1}) and drying with a stream of nitrogen. The wafers were then hydrogen-passivated by being immersed in nitrogen-sparged 40% NH_4F for 15 min and were rinsed with water and dried in a stream of nitrogen. The cleaned and hydrogen-passivated wafers were then brought into a nitrogen-atmosphere glovebox. A monolayer film of **1** was prepared by immersing the Si(111) surfaces in a solution of 0.5 mM **10** in anhydrous CH_3CN in the glovebox for the desired reaction time. After the reaction, the substrates were brought out of the glovebox, rinsed with acetonitrile, and dried with a stream of nitrogen. See Table 1 for the reaction conditions. The film thicknesses were measured with ellipsometry and compared with the molecular length, to confirm that monolayer films were formed.

Surface Reactions. *Reaction of Film **1** on Si(111) with MsCl and Pyridine.* To an oven-dried vial and a magnetic stirbar were added the Si(111) chip with film **1**. The vial was then sealed with a rubber septum, evacuated, and back-filled with nitrogen (3×). Pyridine (2 mL) was added with stirring such that the stirbar did not hit the chip, and the vial was cooled to about −30 °C using a dry ice/CH_3CN bath. MsCl (0.5 mL) was then added to the vial dropwise. The reaction mixture was then warmed to room temperature and stirred overnight. The chip was then taken out, washed copiously with water, CH_2Cl_2, and water, and dried under a stream of nitrogen.

*Reaction of Film **1** on Si(111) with MsCl and **3**.* To an oven-dried vial and a magnetic stirbar were added the Si(111) chip with film **1**. The vial was then sealed with a rubber septum, evacuated, and back-filled with nitrogen (3×). A solution of **3** (10 mg) in $CHCl_3$ (2 mL) was added, and the vial was cooled to about −30 °C using a dry ice/CH_3CN bath. MsCl (0.5 mL) was then added to the vial dropwise. The reaction mixture was then warmed to room temperature and stirred overnight. The chip was then taken out, washed copiously with water, $CHCl_3$, and water, and dried under a stream of nitrogen.

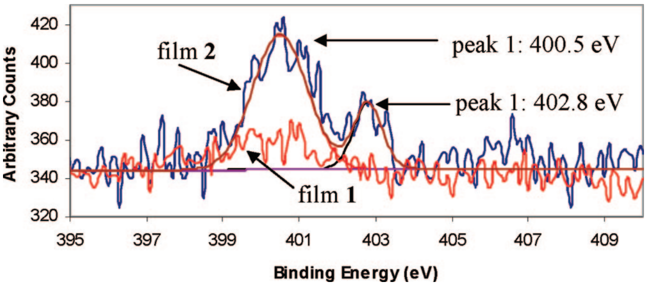


Figure 1. XPS results for N 1s in film **1** (red line) and film **2** (blue line). There are two N 1s peaks for film **2** from deconvolution: 400.5 and 402.8 eV. The signal at around 400.5 eV from film **1** is close to the noise level and is probably due to adsorbed nitrogen.[27] The smooth lines are the fitted curves.

Table 2. Atomic Concentrations of Carbon and Silicon and the Ratio of Carbon to Silicon in Films 1 and 4

sample	C 1s	Si 2p	C:Si
film **1**	33.1	66.9	0.5:1.0
film **4**	64.3	35.7	1.8:1.0

*Reaction of Film **5** on Si(111) with Isoamyl Nitrite and Pristine Fullerene To Form Film **7**.* A freshly prepared Si(111) chip with film **5** on the surface was immersed in 1 mL of CH_3CN in a vial. One drop of isoamyl nitrite was added into the vial, and the mixture was incubated for 30 min. The solution was decanted from the chip, and a fullerene methylene chloride solution was added to the vial. The vial was sealed and placed in the dark for 16 h. Two sets of control tests were done with the same procedures: one control was done without adding isoamyl nitrite and the other was done without adding fullerene. The film thickness before and after each reaction was measured with the ellipsometer, and XPS data were collected to compare the atomic concentrations of the components in the films.

*Reaction of Film **8** on Si(111) with Octacarbonyldicobalt To Form Organometallic Film **9**.* Octacarbonyldicobalt was brought into a nitrogen-filled glovebox and dissolved in anhydrous CH_2Cl_2. A substrate with film **8** was immersed in the solution for 20 h in the dark. The substrate was taken out of the glovebox, rinsed with CH_2Cl_2, and dried with nitrogen. A control experiment was done using a hydrogen-passivated Si(111) surface without the film. Ellipsometry and XPS data were collected on the fresh samples.

Results and Discussion

Reaction of Film 1 with MsCl and Pyridine. XPS analysis was performed on films **1** and **2** under the same conditions to compare the N 1s signal intensities. As shown in Figure 1, the N 1s signal in film **1** is very low, in amounts similar to that for surfaces in which nitrogen is adsorbed from the air.[27] On the basis of the deconvolution of the curve, two peaks are shown in film **2**, with binding energies of 400.5 and 402.8 eV, respectively. The N 1s peak at 400.5 eV is attributed to neutral N in the pyridine structure (due to

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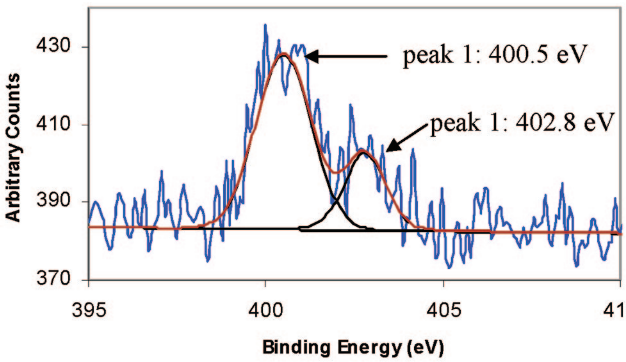

Figure 2. XPS result for N 1s in film **4**. There are two N 1s peaks for film **4** from deconvolution: 400.5 and 402.8 eV. The smooth lines are the fitted curves.

Table 3. Thickness (nm) of the Films before and after Treatment in Acetonitrile

sample	before treatment[a]	after treatment[b]	thickness change
control film **5**, to which no fullerene was added	1.9	2.3	0.4
film **7**		2.9	1.0

[a] The calculated film **5** thickness is 1.9 nm. [b] The measured values are the average of three identically prepared samples with ca. ±0.2 nm error.

Table 4. Atomic Concentrations of Carbon and Silicon and the Ratio of Carbon to Silicon in Films 5 and 7

sample	C 1s	Si 2p	C:Si
film **5**	50.9	49.1	1.0:1.0
film **7**	62.4	37.6	1.7:1.0

physisorbed species) while the N 1s peak at 402.8 eV is attributed to positively charged N^+ in the structure.[28,29] These spectra indicate that the transformation of **1** to **2** on the surface was successful. Film **2** with the positively charged N could have a major effect on the electronic properties of the silicon surface to which it is attached.

Reaction of Film 1 with MsCl and 3. The covalent attachment of **3** to the film surface was confirmed by both the atomic concentrations of C 1s and Si 2p from XPS measurements on films **4** and **1** and the N 1s signal of film **4**. Before the fullerene attachment, the ratio of C to Si concentrations was 0.5:1.0 as listed in Table 2. After the reaction, this ratio increased 3.6 times to 1.8:1.0. This is a result of the surface fullerene coverage and detection of the fullerene carbons.

Similar to the spectra in Figure 1, the N 1s signal in film **4** shows two peaks at 400.5 and 402.8 eV, corresponding to neutral N and positively charged N, respectively, in the film, as shown in Figure 2.

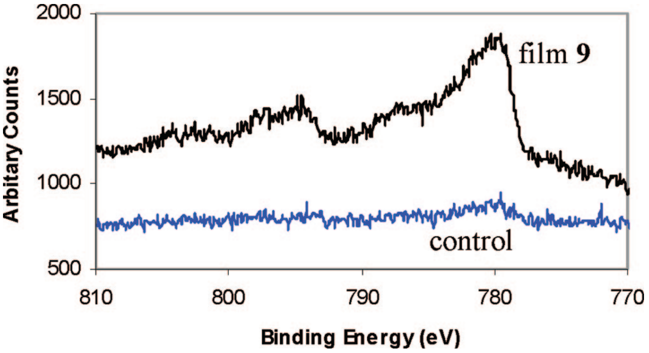

Figure 3. XPS results for Co 2p in film **9** (black line) and the control sample (blue line).

Reaction of Film 5 with Isoamyl Nitrite and Pristine Fullerene. The formation of film **7** was confirmed by both the ellipsometry film thickness measurements and the carbon to silicon ratio analysis from XPS analysis. As listed in Table 3, the film thicknesses for both the control (film **5**, to which no fullerene was added) and sample (film **7**, to which fullerene had been added) increased because of the change of N and K values of the substrate. However, the difference between the thickness of treated film **5** and fullerene-treated film **7** is 0.6 nm, which is close to the diameter of the fullerene molecule of 0.7 nm. Taking into account the bond length of the N−H bond on the end of film **5** (Scheme 3), the thickness difference strongly supports the fullerene molecule existence on the surface of film **7**.

Similar to the formation of film **4** (Scheme 2), there is a significant increase in the ratio of carbon to silicon on the surfaces after the reaction, as listed in Table 4.

Reaction of Film 8 with Octacarbonyldicobalt To Form Organometallic Film 9. The XPS analysis shows a Co 2p signal on film **9**; there was a small amount of cobalt on the control, which resides in the noise region (Figure 3). The formation of film **9** cannot be verified by ellipsometry because the film thickness increase should be <2 Å. However, the XPS analysis (Figure 3) gives strong evidence that the formation of film **9** was successful.

Conclusion

Thin films formed from aromatic organic compounds on Si(111) were modified using surface chemistry to form polar films as well as films containing fullerene and organometallic functionality. The products were analyzed using ellipsometry and XPS, the data of which supported the success of the chemistry. This work is leading to applications in molecular electronics, where the silicon/molecule interface is critical for device responses.[7,30]

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