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Monolayer of Hydrazine Facilitates the Direct Covalent Attachment of C₆₀ Fullerene to a Silicon Surface

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Abstract

The development of oxygen-free organic–inorganic interfaces has led to new schemes for the functionalization of silicon surfaces with nitrogen-based chemical groups. However, building layers of large structures directly on this functionalized surface has remained elusive. This work confirms the path to form a stable interface between silicon and buckminsterfullerene C₆₀ based on covalent chemical bonds. The starting point for this modification is the hydrazine-reacted Si(111) surface with the diamine functionality, which is further reacted directly with the C₆₀ molecules. The chemistry of this process is confirmed spectroscopically and microscopically and can be used to form organic–inorganic interfaces separated by a single layer of nitrogen.

Graphical Abstract

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Notes

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Supporting Information

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Si 2p XPS spectra of a H-Si(111) surface, hydrazine-Si(111) surface, and C₆₀-modified Si(111) surface, full reference for ref 31, and summary of computational studies of the initial steps in the fullerene C₆₀ reaction with the hydrazine-Si(111) surface (PDF)

1. INTRODUCTION

C₆₀ fullerenes have become important building blocks in science and technology and a key direction in nanotechnology research. Because of their properties, especially high electron affinity and a superior ability to transport charge, C₆₀ fullerenes have contributed greatly to a number of applications in energy conversion and solar cell technology,^{1–3} hydrogen gas storage,⁴ sensing,^{4,5} and optics.^{4,6}

Among hundreds of studies of C₆₀ fullerenes, great effort has been devoted to interfacing C₆₀ with semiconducting surfaces, silicon surfaces in particular, seeking novel electrically addressable and switchable functional devices,^{7,8} because the electronic properties of silicon could easily be tuned,⁹ and more importantly, silicon-based devices could be directly integrated within existing electronic circuitry.¹⁰

In the past 20 years, different methods for grafting fullerenes and fullerene-based derivatives have been successfully explored on silicon surfaces. Moro et al.¹¹ studied silicon carbide formation by annealing C₆₀ films (about 200–300 nm thick) deposited on the silicon wafers of up to 900 °C in a high-vacuum (HV) chamber. A more recent report shows that, in an ultrahigh vacuum (UHV) system, a C₆₀ monolayer film was formed on Si(111) by depositing C₆₀ molecules at room temperature (RT) via the thermal evaporation of C₆₀ powder.²¹ Instead of using complex equipment, spin casting was proposed as a convenient route for preparing C₆₀ nanostructures on flat silicon wafers. Feng and Miller¹³ reported the self-assembly of C₆₀ molecules by typically casting C₆₀ solution onto a Si(100) substrate to form about 5–500 monolayers of C₆₀. More recently, Jeong et al.¹⁴ prepared C₆₀ nanoislands with various sizes and heights on silicon wafers using a spin-coating method, and an additional annealing process revealed that these nanoislands were stable during heating up to 400 °C. Finally, a large number of studies have investigated C₆₀ molecules covalently attached to silicon surfaces through self-assembled monolayers (SAMs). Fabre et al.⁹ reported a C₆₀ monolayer anchored on anthracene-terminated Si(100) surfaces following [4 + 2] Diels–Alder cycloaddition. Our own previous study demonstrated that a fullerene C₆₀ monolayer was attached to 11-amino-1-undecene self-assembled monolayers on a Si(111) surface.¹⁵ Despite the fact that long-alkyl-chain organic layers do lead to the formation of C₆₀ bound to the surface, they also introduce additional carbon- or oxygen-containing functional groups that in turn react with the surface itself, causing surface oxidation and leaving contaminants that affect the interface properties for any further modification protocols. Thus, a well-defined and stable Si–N-based oxygen-free interface could be important from both a fundamental and an applied standpoint.

Since Tian et al.¹⁶ reported a wet chemistry approach to preparing a Si(111) surface terminated with the –NH– functionality, searching for organic–inorganic interfaces involving silicon as a starting platform that utilizes Si–N linkages as an alternative to more traditional Si–C bonds or Si–O-based interfaces has attracted substantial interest.^{17–20} The resulting functionalized surface has a potential to be used for further chemical modifications based on known chemical reactions. For example, the reactivity of the amine-functionalized silicon surfaces has been explored for thin film deposition^{21–23} and metallic nanostructure formation.^{24,25} At the same time, as mentioned above, the versatility of the primary amine

group in attachment reactions with buckminsterfullerene C_{60} ^{15,26–28} or their derivatives²⁹ has been demonstrated for amine-terminated organic monolayers on silicon^{15,29} or gold substrates,^{26–28} where the direct dissociative attachment of $-NH_2$ to the cage of the carbon structure has been the major reaction pathway. However, the controlled formation of a direct organic–inorganic interface between silicon and carbon structures in a nonvacuum environment has remained elusive.

In this article, we report a simple wet chemistry method for the covalent attachment of buckminsterfullerene C_{60} to a hydrazine-terminated Si(111) surface, according to the scheme shown in Figure 1. The choice of hydrazine to form the first layer instead of previously investigated ammonia^{16,17} and amines^{15,29} offers high stability and controlled reactivity of the resulting functional group.¹⁸ At the same time, the previously attempted approach to produce a chemical functionality on a silicon surface by directly reacting functionalized hydrazine with Cl-terminated silicon resulted in a very low coverage and facile oxidation of the interface.³⁰ Thus, two-step functionalization, where the first step is silicon modification with hydrazine and the second step is the attachment to this prepared platform, should provide a more reliable path for producing the desired interface. The chemical nature and surface topography of the resulting C_{60} -modified Si(111) surfaces are investigated by X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), and atomic-force microscopy (AFM). Density functional theory (DFT) calculations are performed with the Gaussian 09 suite of programs³¹ to predict N 1s core-level energy and to study the stability of surface species formed.

2. EXPERIMENTAL SECTION

2.1. Materials

The silicon samples used for charge-carrier lifetime measurements were float-zone-grown, double-side polished (111)-oriented Si with a thickness of 1000 μm . Phosphorus-doped, n-type single-side-polished Si(111) wafers (Virginia Semiconductor Inc., 1–10 $\Omega \cdot cm$ resistivity, 325 μm thickness) were used as substrates for all other experiments and characterizations. All chemicals were reagent grade or as indicated: nitrogen (Praxair, boiled off from liquid nitrogen), argon (Keen Compressed Gas, research purity), hydrogen peroxide (Fisher, 30% certified ACS grade), ammonium hydroxide (Fisher, 29% certified ACS plus grade), hydrochloric acid (Fisher, 37.3% certified ACS grade), buffer-HF improved (Transene Company, Inc.), chlorobenzene (Acros, 99+%), PCl_5 (Sigma-Aldrich, 98.0%), benzoyl peroxide (Acros, 98.0%), anhydrous hydrazine (98%, Sigma-Aldrich) (*hydrazine is toxic! check MSDS before use*), methanol (Fisher, 99.8%), fullerene C_{60} (Acros, 99.9%), toluene (Fisher, 99.9%), dichloromethane (Fisher, 99.9%), and tetrahydrofuran (THF) (Fisher, distilled from Na/benzophenone). The deionized water used to rinse the surfaces and containers was from a first-generation Milli-Q water system (Millipore) with 18 $M\Omega \cdot cm$ resistivity.

2.2. Experimental Details

2.2.1. Preparation of Hydrogen-Terminated Si(111) Surface—The hydrogen-modified Si(111) surface was prepared by a modified RCA cleaning procedure.^{32–34} The

Teflon beakers and Si(111) wafers were cleaned for 30 and 10 min, respectively, in SC-1 solution, which is freshly prepared by mixing Milli-Q water, hydrogen peroxide, and ammonium hydroxide (volume ratio 4:1:1) in an 80 °C water bath. After rinsing with Milli-Q water, the clean wafers were etched in HF buffer solution for 2 min and rinsed again with Milli-Q water. Then, the wafers were placed in SC-2 solution that was freshly prepared from Milli-Q water, hydrogen peroxide, and hydrochloric acid (volume ratio 4:1:1) for 10 min to grow a silicon oxide layer. After that, the rinsed silicon wafers were etched in HF buffer solution again for 1 min, followed by a 6 min etching process in ammonium fluoride solution to form a well-ordered hydrogen-terminated Si(111) surface.

2.2.2. Preparation of a Chlorine-Terminated Si(111) Surface—A chlorine-terminated Si(111) surface was produced using a well-established procedure by reacting the H-terminated Si(111) crystal with phosphorus pentachloride powder dissolved in chlorobenzene solvent to form a PCl_5 solution, with a trace amount of benzoyl peroxide added as a reaction initiator.^{35,36} This solution was purged with nitrogen gas for at least 30 min to remove gaseous impurities.¹⁶ A freshly generated hydrogen-terminated Si(111) wafer was placed in this solution in an oil bath at 110 °C for 1 h to prepare a stable chlorine-terminated Si(111) sample. Freshly produced samples were kept under freshly distilled THF.

2.2.3. Reaction of Hydrazine with Chlorine-Terminated Si(111) Surface—The freshly generated chlorine-terminated Si(111) sample was transferred to a clean Schlenk flask filled with argon and then evacuated. This fill–evacuate procedure was repeated three times. Anhydrous hydrazine solution was injected into the Schlenk flask, which was placed in an oil bath at 35–38 °C using a clean, dry syringe. The chlorine-terminated silicon wafer was stirred in the anhydrous hydrazine for 1 h to form a hydrazine-modified Si(111) surface.¹⁸ After the reaction, the hydrazine-modified Si(111) surface was rinsed with dry methanol to remove any residues from the surface, dried with argon, and then kept under fresh THF for further spectroscopic investigations.

2.2.4. Reaction of C_{60} with a Hydrazine-Terminated Si(111) Surface—Fullerene C_{60} was dissolved in toluene to create a C_{60} solution with a concentration of either 1 or 0.25 mM. The silicon wafer modified with the hydrazine monolayer was placed in a 25 mL round-bottomed flask filled with this C_{60} solution and then refluxed at 110 °C under N_2 for 48 h. Then the surface was sonicated in toluene for 5 min, rinsed with dichloromethane, methanol, and Milli-Q water several times to remove physisorbed C_{60} , and dried with N_2 before characterization. Each characterization method was repeated on at least three C_{60} -modified silicon samples following this preparation procedure.

2.3. Characterization Techniques

2.3.1. X-ray Photoelectron Spectroscopy (XPS)—XPS studies were performed on a K-Alpha+ X-ray photoelectron spectrometer (XPS) system from Thermo Scientific. The Al $K\alpha$ X-ray source ($h\nu = 1486.6$ eV) at a 35.3° takeoff angle with respect to the analyzer was used for all of the XPS experiments. The survey spectra were collected over the energy range of 0–1000 eV. The high-resolution spectra for spectral regions corresponding to Si 2p, C 1s, Cl 2p, N 1s, and O 1s were collected over the range of 20 eV at 0.1 eV/step, and a pass

energy of 58.7 eV was used. All of the raw data were analyzed by CasaXPS software, with all peak positions and relative sensitivity factors calibrated to the most intense C 1s peak, which was set to have a binding energy of 284.6 eV.^{35–38}

2.3.2. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)—A ToF-SIMS instrument (ToF-SIMS IV, ION-TOF, Münster, Germany) was used to obtain static negative and positive spectra with a 25 keV monoisotopic Bi³⁺ ion beam. The spectra were collected with a mass resolution of $m/m = 9000$, and the area of analysis was $100 \times 100 \mu\text{m}^2$ over 50 scans. All primary bismuth ion fluences were below the threshold of 1×10^{13} ions/cm² for static SIMS. Both positive- and negative-ion spectra were collected, but only negative ion spectra are provided below as they were the most informative. The calibration of ToF-SIMS data was performed using ION-TOF measurement explorer software (version 6.3). The calibration masses were H⁺, H₂⁺, H₃⁺, C⁺, CH⁺, CH₂⁺, CH₃⁺, C₂H₃⁺, C₃H₅⁺, C₄H₇⁺, C₅H₅⁺, C₆H₅⁺, and C₇H₇⁺ in positive mode and H[−], H₂[−], C[−], CH[−], CH₂[−], CH₃[−], C₂[−], C₂H[−], C₃[−], C₄[−], C₅[−], C₆[−], C₇[−], C₈[−], and C₆₀[−] in negative mode.^{29,30}

2.3.3. Atomic Force Microscopy (AFM)—Tapping-mode atomic force microscopy (AFM) was performed at the University of Delaware to investigate the topography of the modified substrates. The instrument used was a Veeco Multimode SPM with a Nanoscope V controller. Tap300Al-G tips (Budget Sensors) with a force constant of 40 N/m and a drive frequency of 300 kHz were used to obtain the images. The images were analyzed using Gwyddion software (version 2.33).³⁹

2.3.4. Charge-Carrier Lifetime Measurements—A WCT-120 Lifetime Tester with a 60 W light power source was utilized to measure the effective minority carrier lifetime. The carrier lifetime is determined at an injection level of $5 \times 10^{13} \text{ cm}^{-3}$. An rf-bridge circuit, which is coupled by a coil to the measured specimen, senses the conductance in terms of permeability. For the measurement, the sample is cut into $2 \text{ cm} \times 2 \text{ cm}$ pieces and covered with a $1 \text{ cm} \times 1.7 \text{ cm}$ aperture. The time dependence of illumination and excess photoconductance of the measured sample are calibrated by a larger-area silicon wafer of the same type, following the small sample size calibration procedure provided by Sinton Instruments.

2.3.5. Computational Details—Density function theory (DFT) calculations were performed with the Gaussian 09 suite³¹ of programs utilizing the B3LYP functional, the LANL2DZ basis set for structure optimization, and the 6-311G+(d,p) basis set^{40–43} to calculate single-point energies and core-level energies for comparison with XPS experiments. A Si₁₇H₂₄ cluster model, which represents two neighboring top silicon atoms on a Si(111) surface terminated with hydrazine, was used. The bottom three layers in this Si₁₇H₂₄ cluster model were fixed at their bulk positions in DFT calculations to avoid unrealistic distortions. The N 1s core-level energy was predicted using Koopmans' theorem for this Si₁₇H₂₄ cluster model based on our previous investigations.^{44,45} All of the models used in this publication are presented in the Supporting Information section.

3. RESULTS AND DISCUSSION

3.1. Confirmation of Fullerene C₆₀ Adsorption on a Hydrazine-Terminated Si(111) Surface by Atomic Force Microscopy

AFM images shown in Figure 2 were collected following the reaction of the C₆₀ solution with the hydrazine-terminated Si(111) surface. The corresponding line profiles are displayed on the right of the figure. As a starting point, the hydrazine-terminated Si(111) surface in Figure 2a shows no nanostructured features at the nanometer scale and exhibits an RMS roughness of 0.28 nm. After reacting with low-concentration (0.25 mM) C₆₀ solution followed by a 5 min sonication, the C₆₀-modified surface in Figure 2b shows a substantial change in surface topography. The silicon substrate now shows a small number of ad clusters with a height commensurate with a single buckyball molecule. The RMS roughness increased to 1.11 nm, and as will be shown further, this image corresponds to a monolayer of C₆₀ covering the hydrazine-modified surface and a few ad molecules on top of this system or possibly on a small number of protruding defect sites. The sonication approach seems to work nicely with buckyballs and does not induce any additional surface oxidation or C₆₀ monolayer desorption in our case. To see the effect of fullerene concentration on the size of the clusters on the surface, a higher concentration (1 mM) C₆₀ solution is used as the reagent, and the resulting images are presented in Figure 2c,d. In Figure 2c, when the sample is washed with a stream of methanol and Milli-Q water with no sonication, the image exhibits the formation of large clusters, up to 12 nm in height, along with increased RMS roughness, which clearly correspond to multiple layers of buckyballs. This is consistent with the agglomeration of C₆₀ molecules into relatively large and stable clusters at a high concentration of solution.¹⁵ To get rid of these additional physisorbed C₆₀ structures on the surface, the sample was sonicated in toluene for 5 min and then rinsed with dichloromethane, methanol, and Milli-Q water several times. As observed in Figure 2d, this sample exhibits essentially the same density of ad clusters as the low-concentration C₆₀-modified surface, with a nearly identical height of the clusters and RMS roughness. The observation is consistent with previous investigations of C₆₀ aggregate formation^{8,28}. In addition, given the similarity of the samples shown in Figure 2b,d, it is expected that their spectroscopic signatures will also be very similar, as confirmed below in the ToF-SIMS investigation. Because the multilayered physisorbed C₆₀ clusters are removed after sonication and rinsing and because the high-concentration C₆₀-modified surface then shows nearly the same surface morphology as that of the low-concentration C₆₀-modified surface, the C₆₀ molecule reacts with the hydrazine-modified silicon surface in a self-limiting manner.

3.2. Confirmation of Fullerene C₆₀ Chemically Bound to the Hydrazine-Terminated Si(111) Surface by Time-of-Flight Secondary Ion Mass Spectrometry

To identify the structure of the species formed by fullerenes on a surface, ToF-SIMS data are collected for both high- and low-concentration C₆₀ solution-treated surfaces and C₆₀ powder itself for comparison. The negative ion m/z range of 719.5 to 722.5 is displayed in Figure 3. Compared to the spectra of pristine C₆₀ powder, the hydrazine-terminated Si(111) surface treated with C₆₀ solution at either high or low concentration shows identical characteristic features at m/z 720, 721, and 722, as is expected on the basis of the microscopy studies

presented above. Considering that ToF-SIMS is generally regarded to be a semiquantitative technique, the signal intensities have been calibrated to be shown on the same scale. Although here it is impossible to distinguish the peaks at m/z 721 and 722 to be $[\text{C}_{60}\text{-H}]^-$ and $[\text{C}_{60}\text{-H}_2]^-$ or C_{60} with different numbers of ^{13}C isotopes, they are still the strongest evidence that confirms the existence of C_{60} on the C_{60} solution-treated surface. Figure 4 presents a summary of the other relevant spectral ranges studied by this surface analytical technique. Negative ion m/z ranges of 733.6 to 734.5, 747.6 to 748.4, 761.6 to 762.4, and 831.5 to 832.5 are carefully studied and summarized in this figure. Close-up images of the $[\text{C}_{60}\text{-N}]^-$, $[\text{C}_{60}\text{-N}_2]^-$, and $[\text{C}_{60}\text{-N-Si}]^-$ features are displayed in Figure 4a–c with vertical bars indicating the expected positions of corresponding molecular fragments. These results confirm that C_{60} is chemically bound to one or two nitrogen atoms, that the N–N bond of the surface-bound hydrazine remains intact after reaction with C_{60} , and that the formation of a bond between C_{60} and surface nitrogen does not disrupt the presence of the Si–N-based interface. Thus, it is confirmed that C_{60} is chemically attached to the hydrazine-terminated Si surface through the bond formed between the C_{60} cage and nitrogen. It must be pointed out that the presence of three or more nitrogen atoms connected to a fullerene molecule was not confirmed within the signal-to-noise ratio of the current experiments because no noticeable feature was observed in the m/z region of 831.5 to 832.5, as shown in Figure 4d.

3.3. Confirmation of Fullerenes C_{60} Covalently Bound to a Hydrazine-Terminated Si(111) Surface by X-ray Photoelectron Spectroscopy

XPS is used to address the reaction more quantitatively. The studies of the C 1s spectral region following the reaction of C_{60} solution with hydrazine-terminated Si(111) surface are presented in Figure 5. For both the hydrazine-terminated Si(111) surface (Figure 5a) and 1 mM C_{60} solution-modified surface (Figure 5b), three peaks at 284.6, 286.4, and 288.5 eV are discerned and assigned to C–C, C–O/C–N, and C=O bonds. The considerable increase in these peaks is a result of fullerene C_{60} interacting with the hydrazine-terminated silicon surface, forming C–N. Other peaks in this region are more difficult to quantify because of possible adventitious carbon adsorbed on the surface during sample transfer to the XPS instrument. However, the most important observation is the peak at 291.3 eV, which corresponds to the $\pi\text{-}\pi^*$ shakeup in aromatic functional groups,^{46,47} confirming the presence of the aromatic entities on the modified surface following its reaction with C_{60} . Because this peak is not observed for the hydrazine-terminated silicon sample, there is only one possible source of aromaticity in this sample: the presence of C_{60} .

Figure 6 shows the N 1s spectral region of the hydrazine-terminated silicon and C_{60} monolayer on silicon, respectively, along with the DFT-predicted N 1s core-level energies shown as solid bars for the models indicated in the figure. The N 1s experimental spectra shown for the hydrazine-modified Cl–Si(111) surface in Figure 6a indicate a predominant N-containing functionality at 399.6 eV (fwhm = 1.5 eV) and a minor species at 397.5 eV. Previous studies have identified the major peak at 399.6 eV to be Si–NH–NH–Si,^{18,48} with the N–N bond being parallel or nearly parallel to the surface.^{18,48} The minority surface species has been assigned to the N–N bond dissociation, predominantly on surface defect sites,^{16,18} and this assignment is supported by the DFT studies. Figure 6b shows the N 1s region for the sample modified with C_{60} . This spectrum is clearly different from that of the

hydrazine-modified surface. First, the maximum in the main peak is shifted toward higher energy, and the peak itself becomes substantially broader, suggesting that this feature encompasses several different spectral signatures. If the main feature in Figure 6b is fitted with a peak of the same full width at half-maximum as the main feature on the hydrazine-terminated silicon surface (399.6 eV, fwhm = 1.5 eV), then the remaining intensity of this feature can be fitted with a peak at 400.3 eV. Its area is nearly double that for the feature at 399.6 eV. The peak at 400.3 eV (fwhm = 1.6 eV) can be assigned to the nitrogen atoms connected to silicon and the C₆₀ cage. This assignment is made on the basis of the comparison of the experimental spectra with the core-level shifts predicted for the models indicated in Figure 6 for the C₆₀ molecule bound to either one or two nitrogen atoms of the surface-bound hydrazine functionality. It is also fully consistent with the previous investigations of amino-modified buckyballs.^{26,28,29}

Thus, the feature at 399.6 eV in Figure 6 belongs to the unreacted nitrogen-containing surface sites; the peak at 400.3 eV corresponds to the nitrogen atoms connected to silicon and the C₆₀ cage. This assignment is also supported by the DFT studies summarized in Figure 6. This work suggests that the attachment of C₆₀ to either one or two surface –NH functionalities is expected to shift the N 1s level toward a higher binding energy, with reacted N shifting by 0.8–0.9 eV and the unreacted nitrogen atom of the same functional group shifting by 0.4 eV. The positions of the computationally predicted values in Figure 6 are relative to the peak predicted for the hydrazine-terminated silicon surface (Si–NH–NH–Si) that was matched with the experimental value. The minor peak at 397.9 eV in Figure 6b is possibly a combination of the N–N dissociated minority sites on the hydrazine-modified surface and the structure with N atoms inserted into the C₆₀ cage directly, forming pyridine-like N^{49,50} or C–N–C^{49,50} entities. It is investigated by comparing with DFT studies of a proposed structure for a hydrazine-terminated surface and of two possible structures that could exist following C₆₀ modification, as models presented in Figure 6. The minor peak on the hydrazine-terminated surface (397.5 eV) shifts by 0.4 eV toward a higher-binding-energy region after reaction with C₆₀ (397.9 eV). This observation is fully consistent with the result of the DFT prediction mentioned above, which demonstrates that the reaction of minor surface species with C₆₀ leads to the upward shift in binding energy.

On the basis of this comparison, it can be inferred that the chemical reaction has occurred and the observed binding-energy shift is explained by the C₆₀ reaction with the hydrazine-modified silicon surface. More importantly, this simple analysis confirms that approximately two-thirds of surface nitrogen atoms are affected by this reaction, meaning that the high coverage of C₆₀ is formed on this surface. In other words, this observation reinforces the qualitative results offered above by AFM and ToF-SIMS investigations. The AFM studies are indeed consistent with a full monolayer of C₆₀ molecules with the observation of a very low coverage of *additional* ad atoms (or ad clusters) of the buckyballs on top of this first layer or possibly on defect sites. The ToF-SIMS work confirms that the species observed in AFM are bound to the surface covalently, with carbon atoms connected to silicon atoms via a nitrogen bridge and with some buckyballs connected to at least two surface nitrogen atoms. Finally, XPS studies suggest that the reported chemistry is very efficient, with nearly two-thirds of the nitrogen atoms of the hydrazine-modified silicon surface affected by the presence of the C₆₀ cage of the buckyballs: this assessment is made on the basis of the peak

ratio of the nitrogen species affected by the C₆₀ reaction (400.3 eV) to unreacted nitrogen-containing species (399.6 eV). This last observation also implies a very high coverage of the buckyballs within the monolayer.

3.4. Surface Recombination Velocity Measurements of the C₆₀-Modified Si(111) Surface

Charge-carrier lifetime measurements are conducted to evaluate the electronic properties of this C₆₀-modified silicon surface. Table 1 shows the minority carrier lifetime of Si(111) surfaces following the reaction and respective surface recombination velocities. The surface recombination velocity (S) can be expressed by the following equation

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{bulk}}} + \frac{2S}{W}$$

where τ_{eff} is the effective minority carrier lifetime, τ_{bulk} is the minority carrier lifetime within the bulk, and W is the thickness of the silicon wafer (1000 μm). The surface recombination velocity can be calculated by assuming that the bulk lifetime τ_{bulk} is infinite for float zone intrinsic wafers. The absolute values summarized in this table are not as significant as the relative comparison of the same samples at different modification steps because of the possible effects of a relatively small sample size. Nevertheless, the data are consistent with the previous studies of the H-terminated Si(111) reported by our group,⁵¹ but more importantly, it is clear that the hydrazine-terminated Si(111) surface reacted with C₆₀ solution exhibits the lowest minority carrier lifetime and the highest surface recombination velocity. This observation is fully consistent with the C₆₀ molecules serving as efficient electron (and exciton) traps.^{3,4} It can be noted that minor surface oxidation is recorded after the 48 h C₆₀ solution treatment as presented in Figure S1 of the Supporting Information section; however, detailed studies of the effect of surface oxidation versus the attachment of C₆₀ molecules on the charge-carrier lifetime require further investigation. The C₆₀-modified silicon surface exhibits a substantially lower minority carrier lifetime than the silicon oxide surface, regardless of minor surface oxidation during the reaction. This number is actually much lower than the previously reported charge-carrier lifetime measurements for C₆₀ thin films,⁵² but this comparison requires further investigation.

4. CONCLUSIONS

In this work, a novel method to covalently attach buckminsterfullerene C₆₀ to a Si(111) surface has been developed and shown to yield high coverage for a C₆₀ monolayer. The XPS study confirms that the reaction has occurred through the surface Si–NH– functionality. AFM investigations suggest that a monolayer of C₆₀ could be formed on this surface with only a few ad molecules on top of this monolayer or at defect sites. ToF-SIMS results indicate that the nitrogen atom of the hydrazine-modified silicon surface is attached directly to the C₆₀ cage following the surface reaction. More evaluations of this C₆₀-modified silicon surface, including C₆₀ triplet-state lifetime measurements, which lead to potential future applications, are currently under investigation. This unique silicon surface with C₆₀ directly attached to silicon through a single amino functionality circumvents the need for

functionalized organic monolayers formed by hydrosilylation as a starting point for attachment, it avoids the need for ultrahigh vacuum and the formation of Si–C bonds susceptible to oxidation, and it can serve as a platform for further modification based on the chemistry of C₆₀ fullerenes.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Reaction scheme to form a stable interface between C₆₀ fullerenes and a silicon surface.

Figure 2.

Left panels: AFM images of (a) a hydrazine-terminated Si(111) surface; (b) a hydrazine-terminated Si(111) surface reacted with 0.25 mM C_{60} solution; (c) a hydrazine-terminated Si(111) surface reacted with a 1 mM C_{60} solution and washed without sonication; and (d) a hydrazine-terminated Si(111) surface reacted with 1 mM C_{60} solution and washed with sonication to remove multilayered physisorbed C_{60} . Right panels: corresponding line profiles of the images.

Figure 3.

Negative ion ToF-SIMS spectra of the $[C_{60}]^-$ species m/z range following the reaction of C_{60} with a hydrazine-terminated Si(111) surface. The exact positions of the expected ions are shown as solid bars underneath the experimental data.

Figure 4.

Negative ion ToF-SIMS spectra of representative spectral regions following the reaction of C_{60} with a hydrazine-terminated Si(111) surface: (a) $[C_{60}\text{-N}]^-$ species m/z range; (b) $[C_{60}\text{-N}_2]^-$ species m/z range; (c) $[C_{60}\text{-N-Si}]^-$ species m/z range; and (d) $[C_{60}\text{-N}_4\text{-Si}_2]^-$ (or $[C_{60}\text{-N}_6\text{-Si}]^-$, $[C_{60}\text{-N}_8]^-$) species m/z range. The exact positions of expected ions are shown as solid bars underneath the experimental data.

Figure 5. High-resolution XPS spectra of the C 1s region for (a) the hydrazine-terminated Si(111) surface and (b) the hydrazine-terminated Si(111) surface reacted with 1 mM C₆₀ solution.

Figure 6. High-resolution XPS spectra of the N 1s region for (a) the hydrazine-terminated Si(111) surface and (b) the hydrazine-terminated Si(111) surface reacted with 1 mM C₆₀ solution. The core-level energy shifts predicted by DFT for the model systems presented in the figure are shown as solid bars.

Table 1

Charge-Carrier Lifetime and Surface Recombination Velocities for a Si(111) Surface Following the Reaction Scheme^a

surface structure	charge-carrier lifetime, τ (μ s)	surface recombination velocity, S (cm s^{-1})
(a) Si(111)-H	35.1 ± 1.1	1426.7 ± 43.0
(b) Si(111)-Cl	39.9 ± 0.8	1254.5 ± 24.1
(c) Si(111)-NH-NH	10.4 ± 0.9	4821.7 ± 432.1
(d) Si(111)-(NH)N-C ₆₀	3.4 ± 0.1	$14\,599.8 \pm 313.8$

^a(a) Hydrogen-terminated Si(111) surface, (b) chlorine-terminated Si(111) surface, (c) hydrazine-terminated Si(111) surface, and (d) hydrazine-terminated Si(111) surface reacted with 1 mM C₆₀ solution.