

Electrochemical Formation of Close-Packed Phenyl Layers on Si(111)

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4-NO₂ and 4-Br benzenediazonium salts have been electrochemically reduced on H-terminated Si(111) electrodes. Electrochemical measurements evidence that the reaction results in a robust modification of Si(111) surfaces. XPS shows that organic films are monolayer thick and that covalent ≡Si–Ar bonding occurs, with no oxide at the interface. In the case of the Br salt, quantitative RBS measurements suggest that layers are (2×1) close-packed and assess their stability against several rinsing procedures including exposure to 40% HF. A mechanism of grafting is discussed.

1. Introduction

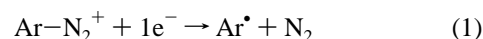
Well-defined organic layers deposited on top of solid surfaces are currently intensively investigated for their potential technological applications,¹ among which sensors are particularly important.^{2–4} Self-assembled monolayers (SAMs) are nearly perfect ordered organic films which are easily obtained by adsorbing alkanethiols on surfaces of noble metals (gold, silver, and copper)⁵ or by reacting alkyltrichlorosilanes with hydroxylated surfaces like SiO₂ or Al₂O₃.⁶ The formation of well-ordered organic layers *directly* in contact with a semiconductor seems less obvious and has been much less investigated, although a direct coupling, between an organic and an electronic materials, should prompt new opportunities.⁷

Alkanethiol layers have been adsorbed on GaAs to prepare patterns with 10–20 nm dimensions using either electron beam or STM-assisted nanolithography.⁸ The passivation of GaAs has been also attempted with various thiols.⁹ Details about the structure of layers were not systematically searched in these studies. To the best of our knowledge, detailed attention to the question of bonding and structure of molecular films has only been addressed with Si(111) surfaces.^{10,11}

The direct coupling of organic molecules with a semiconductor is not as simple as for metals. The process of grafting is not a simple adsorption stage. Common electronic materials, such as Si and GaAs, are covalent materials and their surface is originally covered by ligands or oxide unless one works in the UHV. A *direct* molecular attachment therefore implies the substitution of these ligands by molecules in a reaction step which, ideally, should not damage the initial microstructure of the surface. The properties of organic films depend in particular on their structural order and therefore on the microstructure, at the atomic level, of the surface underneath. Another important consideration is the nature of bonding. Unlike in the case of metals, *rigid* and *directional* covalent bonds form between the molecules and surface atoms. The structure of organic layers is thereby necessarily in registry with the lattice, and the maximum attainable coverage critically depends not only on the size of molecules relative to that of the surface unit cell but also on the matching between the orientation of surface bonds out of the surface and the hybridization of the linking atom on the molecule.

H-terminated Si(111) surfaces prepared by standard wet chemical treatments in fluoride solutions¹² are among the best substrate to start with because they can be prepared flat at the atomic level and are chemically homogeneous (>99% H monolayer termination). Lindford and Chidsey have recently grown robust monolayers of alkyl chains on such surfaces using radical reactions.^{10,11} The authors initiated the process by decomposition of diacyl peroxides so as to abstract the hydrogen atom sitting on the surface. An alkyl radical in solution, deriving either from the peroxide or the added alkene, binds then to the surface radical Si[•] in a sequence of radical reactions. The obtained alkyl adlayers are (2×1) with the remaining sites occupied by Si–OH groups. Although this does not concern flat surfaces, the work of Chazalviel and co-workers is also quite interesting. The authors showed that an electrochemical technique in anhydrous solvents enables to anodically attach –OCH₃¹³ and –CH₃ groups¹⁴ on p-type porous silicon layers. Consistent with this achievement, isolated molecules of 2-propanol (IPA) have recently been imaged by STM on flat Si(111) in a mixture NaOH/IPA under etching conditions.¹⁵ Images confirmed that the alcoholate group may bind on Si according to an oxidation reaction similar to one involving water. It was also found that the LDOS (local density of states) remained low due to a combination of favorable parameters.

The present work considers a new electrochemical approach to derivatize atomically flat Si(111) surfaces with aryl adlayers. We have used the electrochemical reduction of aryl diazonium salts a technique recently introduced by others to covalently graft thin organic films on glassy carbon, carbon fibers, and highly oriented pyrolytic graphite (HOPG).^{16–21} The process, so far mainly performed in an aprotic solvent, has been described by the reactions



where ≡C designates a carbon atom from the HOPG surface.^{16,17} The success of this original approach relies on the low cathodic overvoltage necessary to generate the aryl radicals. As they are not further electrochemically reduced to Ar^{••},²² the aryl radicals are relatively long-lived and it was observed that they react with a surface to form layers which are about one monolayer thick.^{16–18}

The present paper shows that the reduction of 4-nitro- and 4-bromobenzenediazonium salts in an aqueous acidic HF

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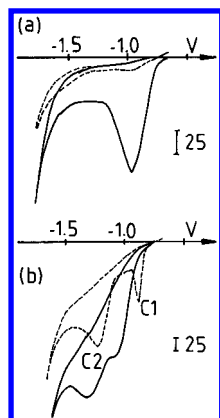


Figure 1. Cyclic voltammetry of n-type H-terminated n-Si(111) in 2 mM solutions of 4-bromobenzenediazonium BF_4^- (a) and 4-nitrobenzenediazonium BF_4^- (b). The supporting electrolyte is 0.1 M H_2SO_4 + 2% HF. Bold and broken lines are first and second cycles. The scan rate was 100 mV/s in (a) and 20 mV/s in (b). The vertical bar is 25 $\mu\text{A}/\text{cm}^2$ in each case.

solution leads to robust modification of Si(111) surfaces. Electrochemical studies and stability tests demonstrate that the films are not adsorbed but covalently attached to the surface. They, for instance, resist to 40% HF. Surface analyses (X-ray photoelectron spectroscopy (XPS), Rutherford backscattering (RBS)) show that the surface is actually modified by a close-packed monolayer of aryl groups attached as $\equiv\text{Si}-\text{Ar}-\text{X}$ ($\text{X} = \text{Br}$ or NO_2). A reaction mechanism is briefly discussed.

2. Experimental Section

Low-doped 1 $\Omega\cdot\text{cm}$ n-type Si(111) samples (purchased from Siltronix, France) were cleaned in trichlorethylene, acetone, and methanol and then chemically etched in HF (1 min) and buffered ammonium fluoride (6 min) so as to prepare atomically flat surfaces terminated by a monolayer of H atoms.¹² An ohmic contact was made on the rear side of the sample by applying an In–Ga eutectic. The solutions were prepared with reagent grade chemicals and bidistilled water. Electrochemical measurements were conducted under potentiostatic mode, with a mercury sulfate electrode (SSE) as reference of potential. All potentials are quoted versus this reference in the following. The solutions were deaerated by bubbling N_2 . The aryl diazonium salts were purchased from Aldrich without further purification. After modification, of the surface, samples were carefully rinsed in water, then acetone and methanol, and water again to remove eventual reaction products and ensure that the modification was not a simple adsorption.

The surface density of bromine atoms was dosed by RBS (Rutherford backscattering) using the 2 MeV Van Graaff accelerator at the Groupe de Physique des Solides (Université Paris 7). XPS measurements were performed with the vacuum SSX-100 spectrometer at ITODYS (Université Paris 7). The monochromated Al K α (1486.6 eV) beam was $\sim 30^\circ$ from the surface. The take off angle for detection was nominally 90° from the surface but could also be at nearly grazing incidence (take off angle 5° – 10°) to increase surface sensitivity. The resolution was typically 0.1 eV. The base pressure in the analysis chamber was $\sim 10^{-8}$ mbar. No electron flood gun was employed. Spectra were fitted with Gaussian profiles using standard procedures.

3. Results

(a) Electrochemical Characterizations. Figure 1 presents cyclic voltammograms obtained with an n-Si(111) electrode in

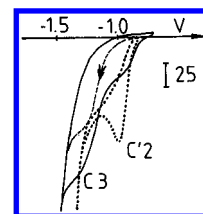


Figure 2. Cyclic voltammetry of n-Si(111) surfaces in 0.1 M H_2SO_4 + 2% HF (80 mV/s). Bold and broken lines are first and second potential sweeps for a surface modified in the $^+\text{N}_2\text{ArNO}_2$ solution. The dotted line is that of an H-Si(111) electrode in the same solution but with nitrotoluene added. The vertical bar is 25 $\mu\text{A}/\text{cm}^2$ in each case.

two 2 mM aryldiazonium solutions in 0.1 M H_2SO_4 + 2% HF. Bold and broken curves are respectively the first and second cycles. In the 4-bromobenzenediazonium tetrafluoroborate ($^+\text{N}_2\text{ArBr}$) solution a reductive wave at -0.95 V is initially observed (Figure 1a) before complete quenching upon further scanning, as if the surface was entirely inhibited. In the 4-nitrobenzenediazonium ($^+\text{N}_2\text{ArNO}_2$) solution the situation looks more complex. The sweep rate was slower than above to evidence the two shoulders at -1.05 and -1.3 V in the first negative going sweep (Figure 1b). Upon further scanning, two sharp peaks C1 and C2 were repeatedly observed at -0.9 and -1.2 V, while the shoulder at -1.05 V completely disappeared.

The electrical charge passed under the two waves at -0.95 V (Br) and -1.05 V (NO_2) found in initial cycles was estimated to be 250 and 375 $\mu\text{C}/\text{cm}^2$, respectively, for the Br and NO_2 compounds. These waves did not reappear even after keeping the sample at rest bias for several minutes. They could be observed again only if the samples were removed from the solution and carefully rinsed in acetone and methanol, which suggests that insoluble or poorly soluble (in water) reaction products are generated during the grafting process (see below).

To check that the surface was actually modified after the first negative going scan as in Figure 1, samples were transferred into 0.1 M H_2SO_4 + 2% HF for further electrochemical studies (the surface was rinsed in the two organic solvents). Figure 2 shows the first and second cycles (bold and broken lines) of an electrode previously modified by reduction of $^+\text{N}_2\text{ArNO}_2$. The first remark is that the I – U curve is notably altered with respect to that of the untreated surface in the same solution. The two peaks C'2 (-1.0 V) and C3 (-1.25 V) are for instance not observed on the H-terminated surface (see Figure 3a, dotted line). There is also a persistent and reproducible cathodic shift of the hydrogen evolution reaction (HER). Together, these observations are primary evidence of the surface modification. They also suggest that the organic film is not simply adsorbed since it resists rinsing in organic solvents.

Looking into more details Figure 2, the comparison of the two cycles shows that peak C'2 disappears and that peak C3 remains from one cycle to the other, though with a slightly decreased amplitude in this case. The dotted line in Figure 2 was recorded on H-Si(111) in 0.1 M H_2SO_4 + 2% HF with a few millimoles of nitrotoluene added to show that peak C'2 can be assigned to the reduction of the nitro group into amino groups on the surface. This observation yields therefore direct evidence that nitro groups are present on the surface. That peak C'2 vanishes *irreversibly* after one cycle is attributed to the irreversible reduction of surface nitro groups into amino groups. The charge under the peak C'2 (bold line) was 78 $\mu\text{C}/\text{cm}^2$. Peak C3 finds no obvious explanation at present.

With the Br compound the corresponding test was meaningless since bromobenzene is reduced at a potential which falls in the HER region. The modification by reduction in $^+\text{N}_2\text{ArBr}$

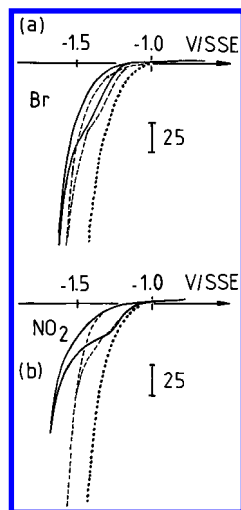


Figure 3. Cyclic voltammetry of Ar-Br (a) and Ar-NO₂ (b) modified electrodes in 0.1 M H₂SO₄ + 2% HF (80 mV/s). Bold curves correspond to as-prepared samples. Curves were identical after exposure of samples to 40% HF for 2 min. Broken lines correspond to modified samples dipped in 10 M NH₄F pH 4.5 for 1 min. Dotted curves are those of the H-terminated surface. The vertical bar is 25 $\mu\text{A}/\text{cm}^2$.

was however evidenced by the negative shift of the HER with respect to the H-terminated electrode (see Figure 3).

To end this electrochemical section, we briefly discuss the assignment of peaks C1 and C2 in Figure 1b. The problem is less obvious than for Figure 2 since the solution contains molecules which may also react at the surface. The reduction of NO₂ into NH₂ being rather slow and involving several intermediate species such as NO and NHOH, we speculate that peak C1 stems from the reduction $\text{NO} \rightarrow \text{NHOH}$, the NO being generated during the first negative going sweep of potential, and that peak C2 is related to the reduction of nitro groups. The fact that peaks C1 and C2 are repeatedly observed in the diazonium solution (Figure 1b) indicates that the reaction involves species in solution.

(b) Tests of Stability. After rinsing in the two organic solvents, the modified samples were exposed to several etching solutions of Si to test the robustness of films. A qualitative test consisted in comparing cyclic voltammograms recorded on thus post-treated surfaces with that of the as-modified electrode. 0.1 M H₂SO₄ with 2% HF was used in Figure 3. All modified samples evidence a cathodic shift of the HER with respect to the n-type H-Si(111) electrode (dotted curve). The shift is maximum on the as-prepared samples (bold lines). That peak C'2 is not observed in Figure 3b comes from the fact that the same sample has already been polarized cathodically to check the response just after modification (this reduced the nitro groups as NH₂, see above).

Figure 3 demonstrates that the Ar-Br and Ar-NO₂ layers are quite stable. After exposure of the modified samples to 40% HF for 2 min, voltammograms were also nearly identical to bold lines. After 1 min in 10 M NH₄F pH 4.5 the *I*-*U* curve remained still nearly unaffected in the case of the Ar-Br layer. The HER was conversely shifted positively, by 180 mV, in the case of the Ar-NO₂ film, suggesting partial removal of the layer. These results, which will be confirmed by RBS in the case of Ar-Br films (see below), pertain to the good stability of adlayers, especially in 40% HF. That the stability slightly decreases in acidic ammonium fluoride probably stems from etching of the substrate through defects in the layer.

(c) XPS Results. The modification of the surface was characterized by XPS after careful rinsing of the samples in acetone

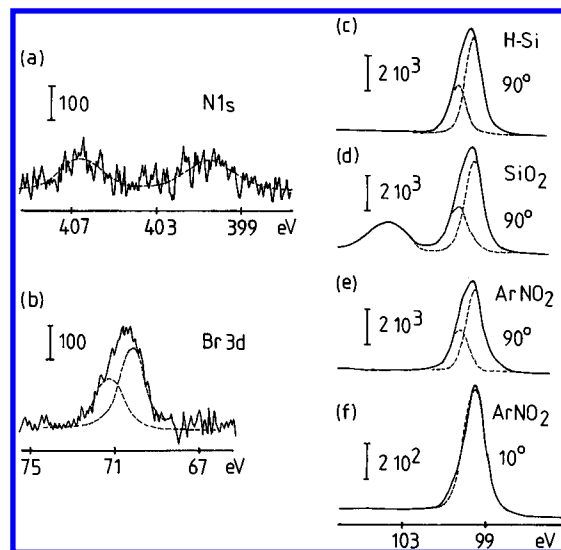


Figure 4. High resolution XPS spectra obtained for the different modified surfaces. The take off angle was 90° in (a-e) and 5°-10° in (f): (a) N 1s peak on the Ar-NO₂ layer; (b) Br 3d peak on the Ar-Br layer; (c) Si 2p peak on the H-terminated; (d) same but after anodization in sulfuric acid (see text); (e-f) Si 2p peak for the Ar-NO₂ modified surface. Grafting conditions: $U = -1$ V for 1 min.

and methanol. Figure 4a,b focuses on the identification of N 1s and Br 3d peaks which are characteristic of the two modifications. The detector was on the surface normal. In the case of Ar-NO₂ grafting, a weak N 1s doublet is resolved (Figure 4a). The peak at 406 eV is a confirmation of the presence of NO₂ groups on the surface (the surface has been coated at a potential of -1.1 V to avoid complete reduction of surface nitro groups into amino groups). Another N 1s peak (400.3 eV) is attributed to contamination and/or other chemical states. No such peaks were found on the test sample. The O 1s (533.2 eV) and C 1s (285.3 eV) peaks were also more intense than on the H-terminated sample (not shown). After Ar-Br modification, the doublet found at 70.7 and 71.8 eV is in good agreement with the Br 3d XPS peak split into Br 3d_{5/2} and Br 3d_{3/2} due to spin-orbit coupling (Figure 4b). The C 1s was also increased and the O 1s peak nearly unchanged with respect to the H-terminated surface. Only a weak N 1s peak at ~400 eV was detected (contamination).

Figure 4c-f compares the Si 2p XPS peaks after different sample preparations. The take off angle for detection of photoelectrons was 90° from the surface, except for Figure 4f where a grazing incidence was used (take off angle 5°-10°). The central energy 99.8 eV of asymmetric peaks is consistent with Si⁰ ground state. Except in Figure 4f, all Si 2p peaks were fitted by two Gaussian (width ~0.9 eV) centered on 100.3 and 99.5 eV which agrees with the doublet Si 2p_{1/2} and Si 2p_{3/2} due to spin-orbit coupling. After anodization in dilute H₂SO₄ at a voltage of 1 V (Figure 4d), the additional broad peak at ~103.5 eV accounts for the ~10 Å thick oxide layer expected under such conditions. After coating with Ar-NO₂, Figure 4e-f provides evidence that the molecular film does not induce any detectable chemical shift, even under conditions where surface effects are maximized with the detector at nearly grazing incidence (Figure 4f).

The ratio I/I_0 of Si 2p XPS peak intensities (modified surface/H-terminated surface) yields insights into the thickness of molecular films. This ratio can be expressed as $I/I_0 = \exp(-d/\lambda \sin \theta)$, with d the film thickness, λ the escape depth of photoelectrons, and θ the take off angle. Using the experimental value $I/I_0 = 0.84$ as in Figure 4c,e ($\theta = 90^\circ$) and taking $\lambda = 40 \pm 5 \text{ \AA}^{23}$ gives a film thickness $d = 7 \pm 0.8 \text{ \AA}$.

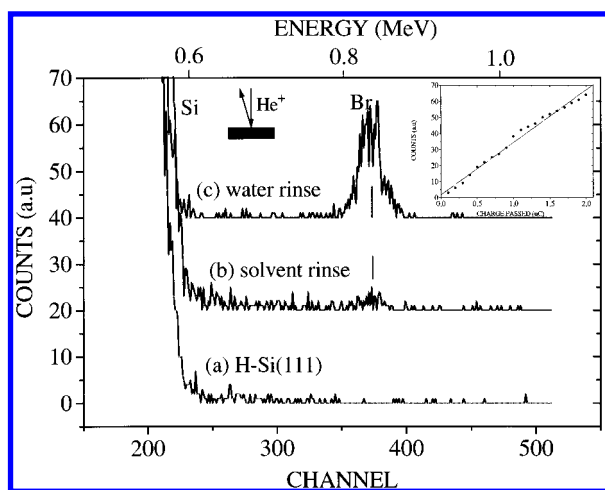


Figure 5. Random RBS yields for an H-terminated Si(111) (a) and two Ar-Br modified surfaces (b and c). The modified sample was rinsed either in organic solvents (b) or in water (c). Grafting conditions: $U = -1$ V for 2 min. Inset: Variations of Br counts as a function of the incident charge in case (b). The sample was moved under the beam after $0.1 \mu\text{C}$ had passed.

This estimate, which holds for both organic films since the ratio of the XPS peak is 0.85 for the Br-Ar layer, is a first element to state that our molecular layers are one *monolayer* thick. The 7 Å thickness is indeed quite close to the vertical dimension of the Ar-X molecules used in this study.

(d) Rutherford Backscattering Measurements. To gain further quantitative insights into the thickness of Ar-Br layers, the surface density of Br atoms was dosed by RBS using a 1 MeV $^4\text{He}^+$ beam, with a detection of particles 165° off the incident beam. Figure 5 shows the random RBS yields obtained on three different Si(111) samples. After grafting in the $^+\text{N}_2\text{-ArBr}$ solution ($U = -1$ V for 1 min) and rinsing in water (curve c), a marked peak accounting for the presence of Br is resolved at the expected energy of 0.83 MeV. After rinsing in methanol and acetone, the peak intensity is however remarkably reduced (curve b). By comparison there are absolutely no counts in this region on the H-terminated sample (curve a).

To further assess that the small peak in curve b is actually due to Br, it was verified that its integral was varying linearly with the incident charge passed. The sample was simultaneously rastered during accumulation (after each $0.1 \mu\text{C}$) to avoid eventual Br losses under the beam. This procedure ensures that the atom density was not underestimated. The inset of Figure 5 shows the result in the case of the modified sample washed in the organic solvents. The straight line yields $(3.7 \pm 0.3) \times 10^{14}$ bromine atoms (Br atoms/ cm^2). For the sample simply rinsed in water, the value is $(2 \pm 1) \times 10^{15}$ Br atoms/ cm^2 , which is a clear confirmation that physisorbed molecules have been removed upon rinsing in the organic solvents.

Similar measurements performed on modified samples (rinsed in the two organic solvents) and then exposed to 40% HF (2 min) or 10 M NH_4F pH 4.5 (2 min) yielded $\sim 4 \times 10^{14}$ Br atoms/ cm^2 , which quantitatively confirms the excellent stability of layers and validates the qualitative test performed in Figure 3. In the case of Ar- NO_2 layers, RBS could not be used since N and O are elements lighter than Si. Nuclear reaction analysis (NRA) measurements are underway to dose the surface density of oxygen and carbon.

4. Discussion

Evidence for the Surface Modification. In analogy with the behavior observed on HOPG,¹⁶ the waves at -0.95 V in the $^+\text{N}_2\text{ArBr}$ solution (Figure 1a) and the shoulder at -1.05 V

in the $^+\text{N}_2\text{ArNO}_2$ solution (Figure 1b) are assigned to the generation of radicals $^*\text{Ar-X}$ by reduction of diazonium cations $^+\text{N}_2\text{ArX}$ ($\text{X} = \text{Br}$ or NO_2). That both features are quenched, as on HOPG, in the second cycle is primary evidence for the surface modification. When grafting is not occurring, as in more diluted solutions, these two waves are indeed repeatedly observed upon cycling the potential.

RBS yields direct evidence that the surface has been derivatized by an Ar-Br layer since Br is detected in Figure 5. Indirect evidence is also supplied by Figure 3a. In the case of Ar- NO_2 layers RBS cannot be used. The identification of electrochemical waves in Figure 2, that is, after transfer of the modified sample in a solution with no diazonium added, may be used to assess the surface modification by an Ar- NO_2 layer. As discussed in the Results section, peak C'2 (Figure 2, bold line) arises indeed from the reduction $-\text{C}_6\text{H}_4\text{NO}_2 + 6\text{e}^- \rightarrow -\text{C}_6\text{H}_4\text{NH}_2$ ²⁴ since it occurs at the same potential where nitrotoluene is reduced on the bare surface (Figure 2, dotted line). After one cycle all nitro groups on the surface are reduced into amino groups which quenches the associated peak in the second cycle (broken line).

Another evidence of the surface modification is given by the wettability of surfaces. After treatment in $^+\text{N}_2\text{ArNO}_2$ and careful rinsing in acetone and methanol, the surface becomes strongly hydrophilic, while the initial H-terminated surface is highly hydrophobic. In the case of the Br compound the difference was less spectacular. Rinsing samples in water instead of organic solvents left the surface rather hydrophobic. This is consistent with the presence of some organic molecules physisorbed on top of the first layer (see model below and Figure 5). Whereas the diazonium salt is relatively soluble in aqueous solution, we indeed infer that the electrochemical inhibition of the surface (Figure 1, broken lines) stems from the formation of insoluble or poorly soluble products generated in secondary reactions. Bromobenzene and nitrobenzene are indeed most probably created (see reaction model below).

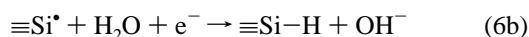
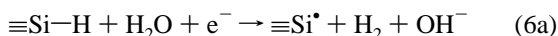
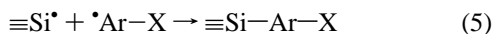
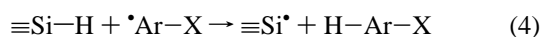
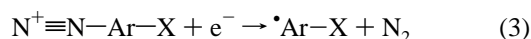
To summarize the above findings: (i) The surface is actually modified by reduction of aryl diazonium salts. The presence of Br is proved by both RBS (Figure 5) and electrochemical transfer (Figure 3). In the case of the 4- NO_2 aryl diazonium compound, the electrochemical test of transfer has identified the presence of NO_2 groups on the surface (Figure 2). (ii) Layers are quite robust since the modification resists the severe rinsing procedure, including exposure to fluoride solutions which etch Si and SiO_2 (see Figure 3). RBS could quantitatively confirm the results in the case of the Ar-Br layer (Figure 5). (iii) The aryl layers are conductive though they delay the HER toward negative potential.

Evidence for Si-C Bonding. Observation (ii) above excludes that the modification of surfaces is a simple adsorption stage and rather suggests a covalent binding of the organic film on Si. The formation of vertical $\equiv\text{Si-phenyl}$ bonds is indeed supported by several facts. The first one is the absence of noticeable chemical shift of the XPS Si 2p (Figure 4), even under experimental conditions where the signal is mainly surface sensitive (detector at grazing incidence as in Figure 4f). The chemical shift for $\equiv\text{Si-Ar}$ is expected to be smaller than 1 eV since XPS tables give a chemical shift of ~ 1 eV for Me_4Si and Ph_4Si . This value is certainly larger than in our situation because the Si topmost atom is only once bound to a phenyl ring instead of four. A strongly electron attractor group like NO_2 should further reduce the charge δ on $\equiv\text{Si}^{\delta+}$. That the aryl groups bind vertically on the surface seems natural when considering the sp^3 hybridization, with one bond vertical, of Si atoms of

(111) terraces and the sp^2 hybridization of the C on aryl groups. A $\equiv\text{Si}-\text{Ar}$ binding is also consistent with the reaction model below.

Other kinds of bonding may in contrast be discarded. The formation of Si–N bonds, by some reaction involving the $-\text{C}\equiv\text{N}^+$ end of the diazonium molecule is for instance unlikely since the triple bond is quite stable. In the same way $\equiv\text{Si}-\text{O}-\text{C}$ bond formation is also unlikely because layers are remarkably stable in 40% HF (Si–O bonds would readily be etched). We also note in Figure 4 the absence of contribution corresponding to oxide or suboxide. No satellite peak is visible between the 99.5 eV (Si^0) and 103.3 eV (energy corresponding to SiO_2), even at grazing incidence.²⁵

Reaction Model. The formation of a monolayer thick aryl molecular films can be rationalized by the following reaction scheme, where $\equiv\text{Si}-\text{H}$ designates an atom of silicon triply bound to the lattice on a (111) terrace:



Reaction 3 is identical to reaction 1 and is well accepted for the generation of aryl radicals ($\text{Ar}-\text{X}$ with $\text{X} = \text{NO}_2$ or Br) in acidic aqueous media.²⁴ Molecular binding stems from a two-step reaction. In reaction 4 a first radical abstracts the H atom from the surface, similar to what has been reported in the case of carbon compounds.^{26,27} The situation is even more favorable here since Si–H bonds are weaker than C–H ones.²⁸ The resulting surface radical $\equiv\text{Si}^\bullet$ may then react with a second aryl radical to generate the $\equiv\text{Si}-\text{Ar}-\text{X}$ bond. Reaction 6 accounts for the cathodic evolution of molecular hydrogen on H-terminated silicon. This is a Heyrovsky mechanism^{29,30} where the above surface radical state $\equiv\text{Si}^\bullet$ is generated. It might also participate in reaction 5 since the grafting process occurs close to the HER. Reactions 3–6 show that at about two electrons are necessary to bind an aryl group which is consistent with previous determinations showing that half of the generated aryl radicals that react are consumed in secondary reactions.²²

According to the reaction scheme, the modification process removes H atoms from (111) terraces, which is verified by preliminary FTIR measurements showing that the stretching mode of $\equiv\text{Si}-\text{H}$ is indeed *partially* quenched after grafting, which suggests that Si–H bonds remain on (111) terraces.³¹ The model predicts that the grafting process is self-stopped after saturation of accessible surface, which is in accordance with Table 1. In a protic solution, the formation of a second layer seems in fact very unlikely since both the NO_2 and the Br on top of the aryl group will not be easily removed from the ring. A reaction of substitution, in ortho position, involving aryl radicals generated in the solution seems also unlikely for steric reasons. Last, we remark that the products of reaction 4 might be responsible for the inhibition of the surface upon prolonged cathodic polarization in the diazonium solutions (Figure 1) since they are poorly (nitrobenzene) soluble or completely insoluble (bromobenzene) in aqueous solutions.

Layer Characteristics. Table 1 summarizes some physical characteristics of aryl layers as derived from the different techniques used in this study. They all conclude to the

TABLE 1: Equivalent Coverage/Thickness of Layers

technique	quantity measured	equiv coverage/thickness
voltammetry	electrical charge:	7.84×10^{14} molecules/ cm^2 ^a
	Br: $250 \mu\text{C}/\text{cm}^2$ NO ₂ : $375 \mu\text{C}/\text{cm}^2$	11.2×10^{14} molecules/ cm^2 ^a
RBS	Br surface density	$(3.7 \pm 0.3) \times 10^{14}$ Br atoms/ cm^2
Si 2p XPS	attenuation I/I_0 : ^b Br and NO ₂ : 0.84	$(7 \pm 0.8) \text{ \AA}$

^a The calculation assume that two electrons are consumed to graft one aryl group (see reaction model). The equivalent electrical charge is therefore $250 \mu\text{C}/\text{cm}^2$ for 1 monolayer on Si(111) [7.84×10^{14} sites/ cm^2]. ^b I_0 is the peak intensity on the H-terminated electrode.

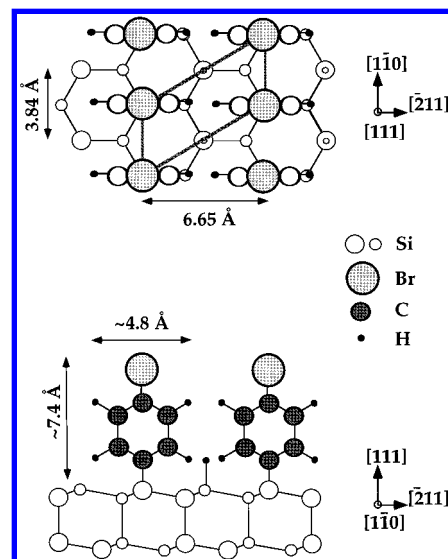


Figure 6. Molecular structure of the (2×1) structure of bromoaryl layers on Si(111). Top (a) and side (b) views.

formation of single monolayer thick films. The value of the attenuation of the Si 2p XPS peak with the take off angle of 90° from the surface is indeed a pertinent parameter to estimate the film thickness and the 7 Å found with both types of molecular films are very close to the geometrical height of the monosubstituted aryl groups used in this study. The formation of a single layer is also consistent with the reaction model discussed above. RBS is quantitatively confirming this estimate in the case of $\text{Ar}-\text{Br}$ films since the Br coverage is about half of a monolayer on (1×1) -Si(111). The equivalent thickness derived from the electrical charge measured under the reduction wave of aryl groups is the least precise determination. Assuming that one molecule is grafted for $2e^-$ exchanged (see reaction model above) the thickness of 1 *full* monolayer [7.8×10^{14} molecules/ cm^2] is certainly overestimated because of the occurrence of the HER and other secondary reactions which are not accounted by the reaction model.

Together, XPS and RBS yield insights into the molecular structure of organic films. The Br coverage being equivalent to nearly half of a monolayer on (1×1) -Si(111) and the film being a *single* monolayer thick (Table 1) we may infer that the aryl layer is (2×1) . The remaining sites are most probably $\equiv\text{Si}-\text{H}$ monohydrides because there is no chemical shift in Si 2p XPS peaks after grafting (Figure 4e–f). FTIR results also support the presence of Si–H bonds between the aryl groups.³¹ Figure 6 presents a (2×1) molecular structure with rings aligned parallel to the $\sqrt{3}$ direction. The same structure has been derived from modelization.³² A few cycles to minimize the total energy of a slab containing two bilayers of Si with seven vertical bromophenyl groups arranged in a (2×1) structure on

top of the surface leads also to rings parallel to the $\sqrt{3}$ direction to reduce van der Waals interactions between rings. The 2-D packing density shown in Figure 6 corresponds to ~ 25 Å²/molecule, a value consistent with previous determinations⁶ and smaller than the maximum packing density derived by others.^{16,17} The same structure is obtained with aryl groups bearing other substituents such as $-\text{NO}_2$ and $-\text{CH}_3$. Work is now in progress to image layers by STM and characterize the long-range order by complementary techniques.

5. Conclusions

In conclusion, *direct* $\equiv\text{Si}$ –phenyl bonding has been achieved by electrochemical generation of aryl radicals in the vicinity of an H–Si(111) surface in contact with an aqueous diazonium solution. The technique has several advantages. (2 \times 1) close-packed layers are easily obtained. That the process is *cathodic* prevents any degradation or oxidation of the surface during surface processing and leaves the remaining sites passivated with hydrogen. The nature of the bonding, through Si–C instead of Si–O bond formation, is also very much interesting for the resistance of layers to chemical etchants of silicon. Work is in progress to further characterize the structural and electronic properties of layers.

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- Alchemy III software. The final energetic parameters leading to the structure in Figure 6 were as follows: bond 15.9 kcal, angle 41.5 kcal, van der Waals, –48.5 kcal, torsion 9.3 kcal, and oop 0.1 kcal for a total energy 18.3 kcal. Each contribution is related to specific forces. A small oop indicates that rings remain planar and small angle and bond contributions mean that bonds and angles are not distorted with respect to expectations. The negative vdW energy certifies that rings are not in contact with each other.