UV-Induced Reaction of Conjugated Styrene Derivatives with H-Passivated Silicon Surfaces

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Abstract

The formation of organic layers on hydrogen-passivated silicon (HPS) surfaces via (UV) ultraviolet treatment was completed for three styrene derivatives with different conjugated lengths. The styrene molecules were synthesized and characterized using nuclear magnetic resonance (NMR) spectroscopy and gas chromatography-mass spectrometry (GC-MS). Layer formation on silicon was then accomplished through the UV irradiation (254 nm) of an HPS surface that had been immersed in a benzene solution of the respective styrene derivatives. NMR and GC-MS were then employed to ascertain that the styrenic molecules still retained their original purity after UV treatment. X-ray photoelectron spectroscopy (XPS) was used to determine the chemical composition and elemental ratio (qualitative and quantitative analysis) of the organic layers on the silicon surfaces. The treatment of HPS with styrenes can serve as a promising method for the formation of covalently attached organic layers on silicon surfaces that can be subsequently modified for interfacing with biologically important molecules.

Introduction

The formation of covalently attached organic monolayers on hydrogen-passivated silicon (HPS) surfaces has attracted much attention from many research groups in the past decade.[1] These monolayers can often act as a protective coating for the underlying silicon substrate.[2] They can also be used to modify and tune the physical and chemical properties of the surface, allowing it to be used in electronic devices, semiconductor technology, biotechnology, and sensing applications.[3] For such applications,[4] these monolayers must ideally possess three specific components: a direct attachment point (double or triple bond) to the Si surface, a conjugated carbon framework of tunable thickness, and a surface functional group (Br or I) that can be further modified to bind/sense more complex molecules.

Organic monolayer formation on silicon surfaces has been achieved via catalyzed,[5] thermal,[6] and photochemical reactions[1] of HPS with organic molecules containing terminal alkene groups. Previous studies have shown that the Si-H bonds on HPS surfaces can serve as a good chemical handle for further modification via reactions with functionalized alkenes using radical initiators,[7] heat,[7] and light.[4] In particular, surface functionalization using light is an attractive strategy to directly photo-pattern a wide variety of organic functional groups (halides, amines, and carboxylic acids) on Si substrates.[8] These functional groups can, in turn, be used to bind to more complex molecules in sensing or device applications.[4] If a conjugated monolayer on HPS can be created from organic molecules, it can serve as a conducting layer on the semiconducting silicon surface and allow for the modulation of electronic conductivity at the silicon/external environment interface.[9] Once these conducting properties are established, further studies involving the sensing of DNA and other biological entities can be carried out by monitoring their interactions with the monolayer.

HPS surfaces readily develop an oxide layer when exposed to air or moisture, however, which makes them difficult to use directly in sensing applications. This oxide layer is nonconducting, does not allow for the efficient transfer of electrons from the external environment into the Si substrate, and is difficult to modify. Not only is the electronic conductivity of the Si surface reduced upon oxide formation, the chemical reactivity and the thickness of the oxide layer are difficult to control, making it increasingly difficult to form a well-defined overlayer of conjugated organics that can electronically interact with the Si substrate.[10] Although SiO_2 can be modified with silyl chloride and siloxane chemistry, there is currently no known method for forming a smooth, tightly packed monolayer of organic molecules on silicon oxide.

The formation of covalently linked organic overlayers on HPS has been shown to prevent the formation of oxide layers on Si surface.[11] If such overlayer is made up of conjugated molecules, it may serve the dual roles of mediator-protector between the silicon substrate and the external environment in a sensing application. These conjugated molecules can impart tunable electronic and chemical properties to the silicon substrate[4] and ensure the existence of a stable silicon surface without an oxide layer. In addition, if the overlayer also bears functionalities that can interact with analytes of interests, systematic studies involving controlled electron transfer through the organic layer can be done. While the conductivity of such an overlayer is known to be affected by the height and structure of the molecule, as well as the density and orientation of the layer, how these parameters can be manipulated is still unknown.[11] Nevertheless, the formation of covalently linked organic overlayers on HPS holds the promise to be atomically flat, tightly packed, and allow for easy attachment of biological molecules, which cannot be otherwise fixed directly onto the Si surface.[11]

The current study aims at elucidating the relationship between the structure of the conjugated molecules and their role in forming overlayers on HPS. In particular, this research reports the controlled formation of styrene-derived organic layers with variable thicknesses on silicon via UV treatment of HPS surfaces.

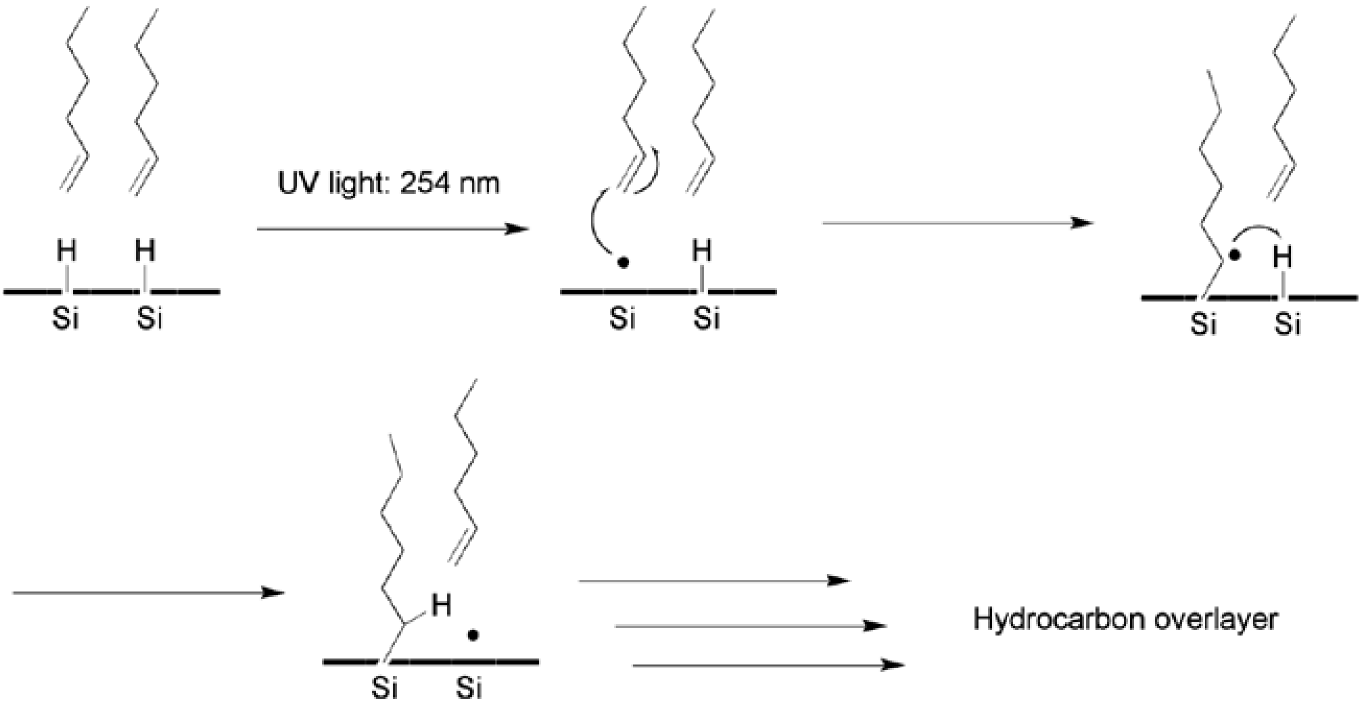

Figure 1. Possible mechanism for organic overlayer formation with terminal olefins on HPS under UV irradiation.

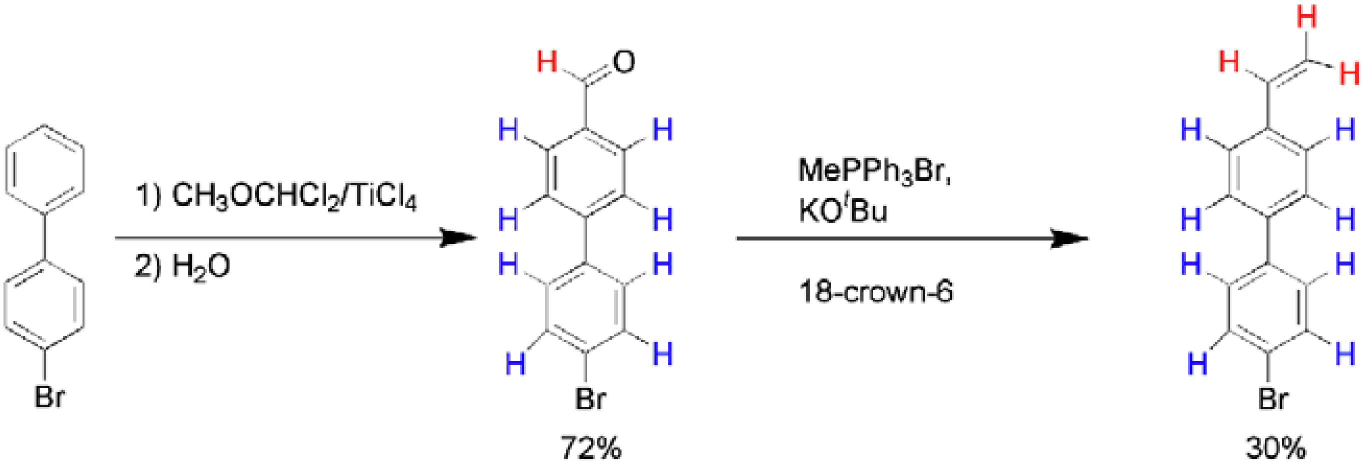

Figure 2. Synthetic scheme for 4-bromo-4′-vinylbiphenyl.

Background

Linford and Chidsey first reported the formation of organic monolayers on HPS via pyrolysis of diacyl peroxides.[12] A subsequent study established monolayer formation via irradiation (UV and visible) of an HPS surface in the presence of a liquid alkene.[13] While alkenes have also been attached to silicon surface at high temperatures (> 140° C),[12] preference has been given to UV irradiation when the alkene is not photosensitive, presumably because such reaction can take place at room temperature and is ideal for any integrated circuit (IC) manufacturing process to avoid thermal budget. The mechanism for photochemical "grafting" of alkene to HPS was proposed by Chidsey and coworkers (Figure 1)[12] to involve an initial generation of Si-based surface radicals (dangling bond). These highly reactive species then react with the alkene monomer at the C=C bond, forming a covalent Si-C bond and a secondary carbon radical. This newly formed carbon-based radical can then interact with an adjacent surface Si-H bond, generating a new active site for the next incoming alkene monomer. The overall radical-chain process establishes UV irradiation as a reliable method for forming overlayers on silicon surfaces.

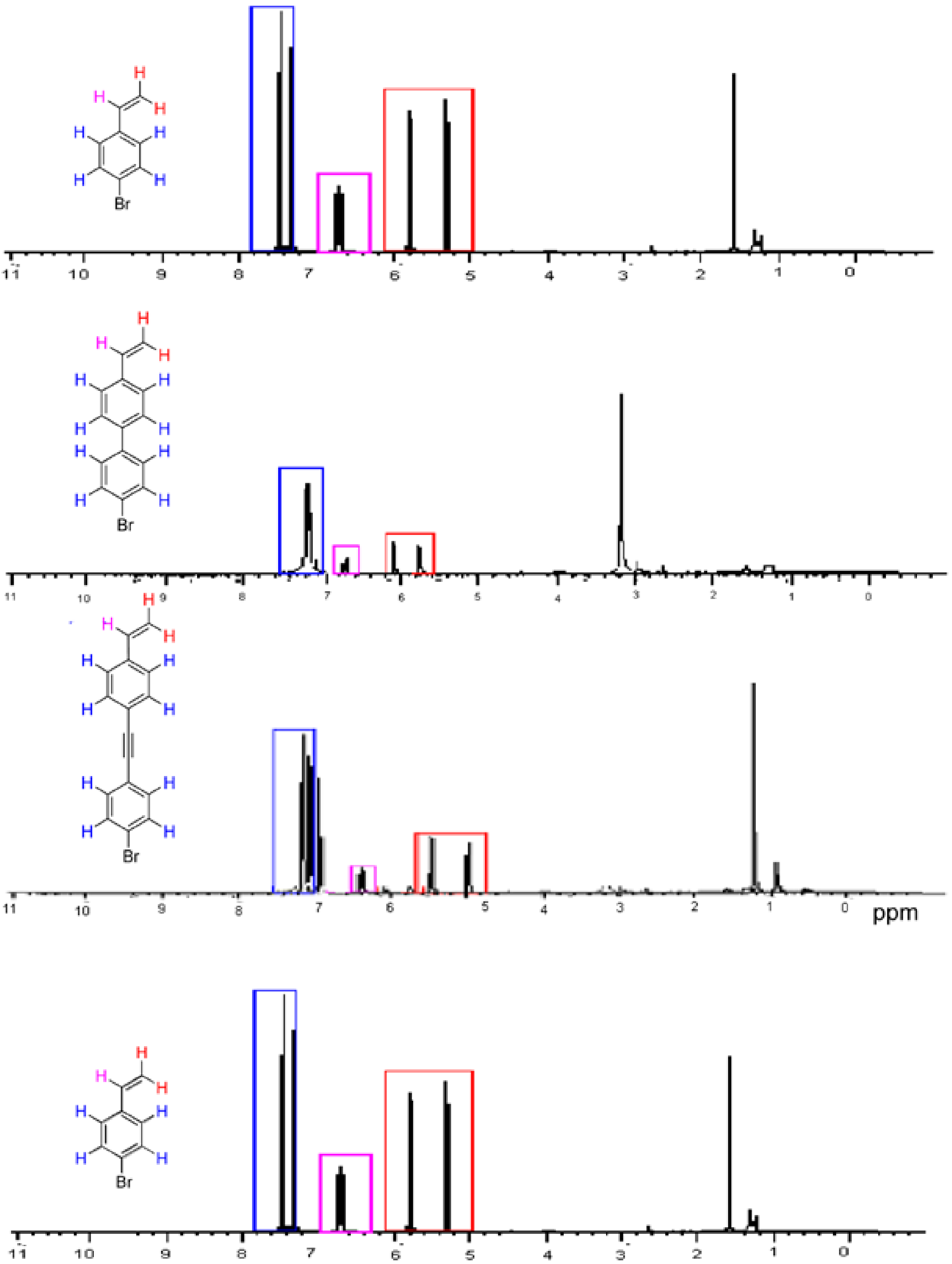

Figure 3. The ^{1}H NMR spectra of 4-bromostyrene (top), 4-bromo-4'-vinylbiphenyl (middle), and 4-(p-bromo ethynylphenyl)styrene (bottom).

Approach

Our approach to prepare and characterize conjugated organic layers on silicon surfaces is composed of two main steps: (1) synthesize and characterize styrene-based conjugated organic molecules, and (2) form organic layers on HPS via UV irradiation and characterize them.

Synthesis and Characterization of Styrene-Based Conjugated Organic Molecules

Three types of conjugated organic molecules with varying lengths were employed in our study: 4-Bromostyrene (~7.1 Å as calculated by Chem 3D software version 4), 4-bromo-4'-vinylbiphenyl (~11.5 Å), and 4-(p-bromo ethynylphenyl)styrene (~14.0 Å). 4-Bromostyrene is commercially available, and 4-(p-bromo ethynylphenyl)styrene was previously synthesized by this group.[14] The synthesis of 4-bromo-4'-vinylbiphenyl was accomplished using a two-step procedure previously report by Dhal (Figure 2).[15] The first step involved a TiC^{l4}-promoted Friedel-Crafts alkylation followed by hydrolysis to obtain the resulting 4-bromo-4'-formyl biphenyl as a shiny brown color powder in 72% yield after flash column chromatography with benzene eluent. The next step involved the Wittig methylenation of this aldehyde intermediate with methyltriphenyl phosphonium bromide and potassium tert-butoxide in anhydrous tetrahydrofuran. To increase the solubility of the base, a catalytic amount of 18-crown-6 (2.7 mol%) was also added. It is also important that the phosphonium salt and base are allowed to react

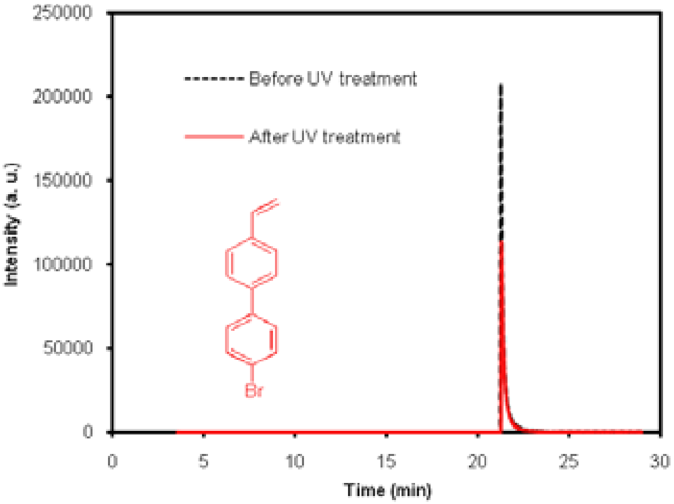

Figure 4. GC traces of the reaction mixture taken before and after UV treatment for 4-bromo-4'-vinylbiphenyl.

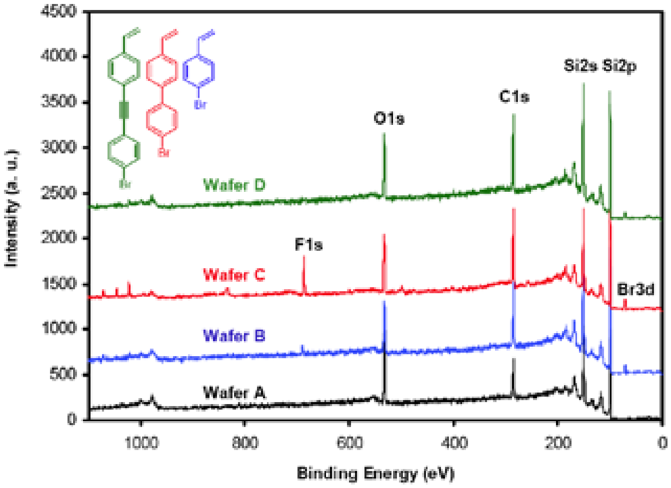

Figure 5. XPS general survey scans for a clean wafer of H-passivated silicon (black) and HPS wafers that have been UV-irradiated in the presence of 4-bromstyrene (blue), 4-bromo-4'-vinylbiphenyl (red), and 4-(p-bromo ethynylphenyl)styrene (green).

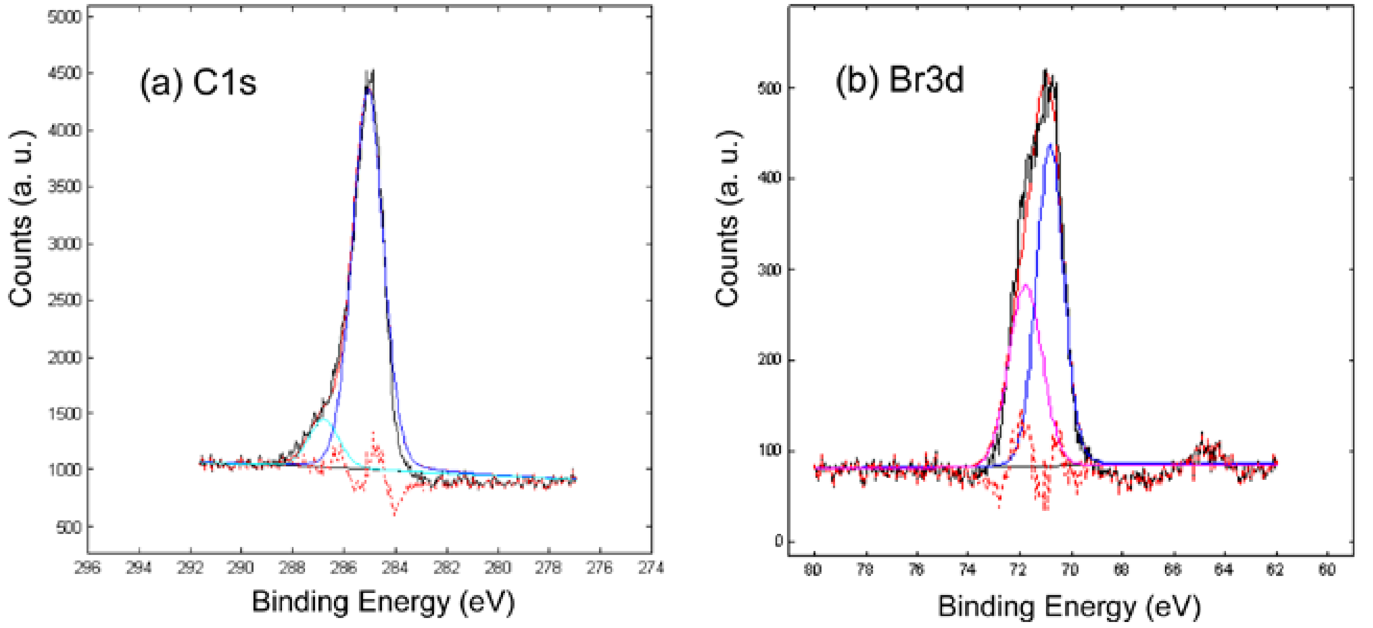

Figure 6. Curve-fitting analyses for the XPS spectra of a wafer that has been UV-irradiated in the presence of 4-bromo-4'-vinylbiphenyl: (a) C1s and (b) Br3d regions.

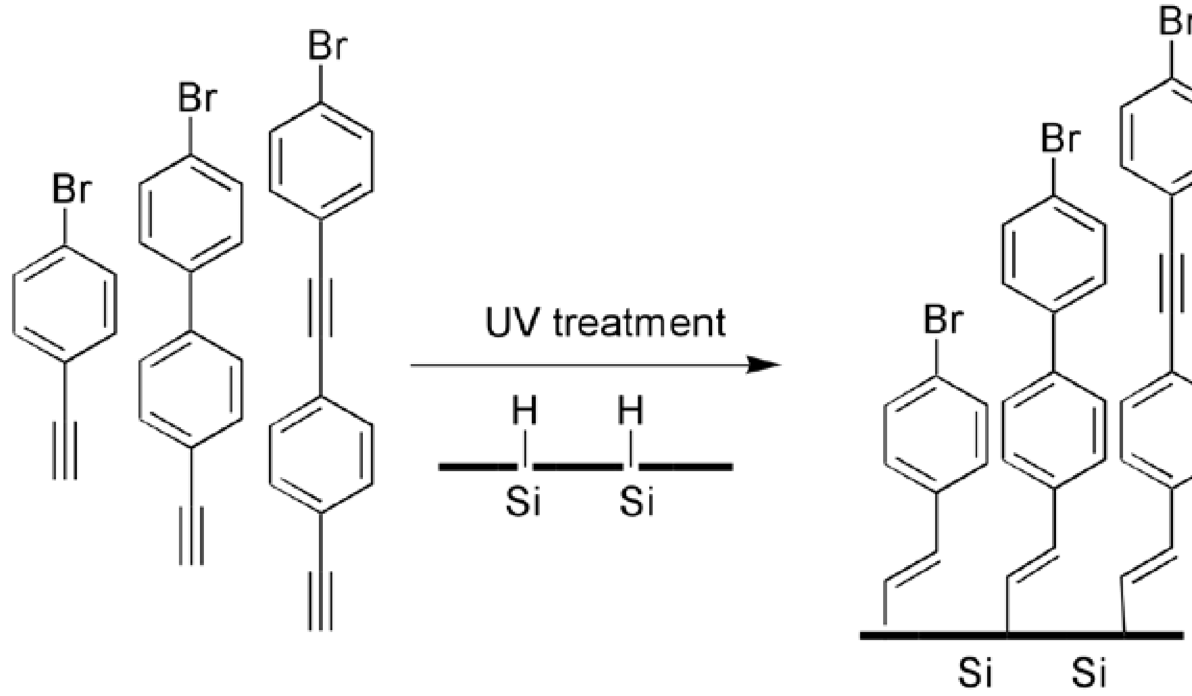

Figure 7. Proposed formation of fully conjugated organic monolayers on HPS wafers starting from organic molecules containing terminal acetylene substituents.

together to form the ylide prior to the addition of the aldehyde. The crude product was extracted with dry ether and eluted thorough a pad of neutral alumina with ether. Evaporation of the combined organics and recrystalization of the resulting solid from isopropanol yield pure 4-bromo-4'-vinylbiphenyl as a light yellow powder. NMR and GC-MS were used to determine the formation of the pure compound.

Formation and Characterization of Organic Layers on HPS

To prepare HPS, the native oxide layer and any impurities present on a commercial silicon wafer (n-type, arsenic doped, resistivity = 0.01 Ωcm, Virginia Semiconductor) was removed through sequential exposure to concentrated solutions of HF, piranha (H_2SO_4/H_2O_2), and NH_4F.[16] This process also enables the formation of a smooth hydrogen-terminated layer on top of the silicon substrate. The resulting hydrogen-passivated silicon wafer (~1.5 cm^2) is then immersed in a 0.2 M benzene solution of the styrene derivative and exposed to UV light (Spectroline 11C-1, Spectronics Corporation, Westbury, New York, 254 nm wavelength) under a nitrogen atmosphere and in a darkened environment for 2 hr. This protocol is relatively easy to set up and is compatible with a wide range of organic molecules because it can be done in solution and at room temperature and pressure.[8]

After the UV irradiation, the organic-functionalized silicon wafers were then rinsed completely in methylene chloride (5 mL), ultrasonicated for 5 min (Fisher Ultrasonic Cleaners, Sonic Cleaner, Model FS6), and stored in a nitrogen-filled glovebox. XPS analysis (Omicron ESCA Probe, Al K∝ radiation, hv=1486.6 eV, takeoff angle of 45° to the detector) was used to confirm monolayer formation on the silicon surface by observing the ratio of atoms present in the overlayer.

Results and Discussion

NMR spectroscopy (Varian INOVA 500 FT-NMR spectrometer, 500 MHz for ^1H NMR) was used to confirm the synthesis of the styrene derivatives and determine their purity (Figure 3). Each NMR spectrum taken for the three organic molecules showed the correct resonances for the benzylic protons (δ 7.40–7.60) and vinyl hydrogens (δ 5.25–5.85 and δ 6.65–6.80) with minimal presence of impurities. (The extra peak present in each of the three spectra at 1.5 ppm is due to water residues.) This verification allowed continuation to the next step, organic layer formation.

GC-MS (Hewlett-Packard 6890 GC/MSD interfaced to a HP 5973 Mass Selective Detector Quadrupole Mass Spectrometer) was used to further verify the identity and purity of the styrene derivatives after isolation. It was also employed in the analysis of the styrene reaction solution after UV treatment to determine if the styrenes had undergone nonpolymer side reactions during overlayer formation. 4-Bromostyrene (the shortest molecule) appropriately had the shortest retention time of 11 min on the GC column, and a molecular mass of 183 g/mol. 4-Bromo-4'-vinylbiphenyl (11.5 Å) had a retention time of 21 minutes with a molecular weight of 259 g/mol. Additionally, 4(*p*-bromo ethynylphenyl) styrene (the longest molecule) showed the longest retention time of 24 min and a molecular mass of 285 g/mol. All three styrene derivatives exhibited two 1:1 mass spectral peaks for the molecular ion, corresponding to the presence of Br. The similarity between each set of GC traces (before and after irradiation) demonstrates that none of the styrene derivatives had undergone nonpolymer side reactions after UV treatment.

Figure 5 shows the XPS general survey scans for a clean HPS surface and three HPS samples that had been exposed to our three styrene derivatives under identical UV irradiation conditions. The XPS spectrum of the clean HPS wafer (wafer A, black line) shows only the presence of C1s (284.5 eV), O1s (532 eV), Si2s (150.5 eV), and Si2p (99.5 eV) signals, indicating a clean surface. The remaining three spectra (wafers B, C, and D) exhibited enhanced C1s signals compared with Si2p, as well as Br3d (70.5 eV) signals that were not present on the clean HPS surface, implying that the styrene-exposed wafer indeed reacted with the bromine-containing styrene derivatives. The XPS spectrum from the reaction between HPS and 4-bromo-4'-vinylbiphenyl (wafer C, red line) also contained an extra peak from fluorine (696 eV), which may be due to residues left over during the etching step.

When wafer C was examined by a detailed XPS scan in the Br region, its Br3d peak matched that of a C-Br (70.5 eV) bond, not a Si-Br (69.0 eV) bond (Figure 6(b)). This result suggests that 4-bromo-4'-vinylbiphenyl reacted with the silicon surface through the vinyl group rather than the C-Br bond. The carbon-to-bromine atomic ratio for this sample was 12:1, slightly low from the theoretical value of 14:1, presumably due to the attenuated sensitivity of the XPS technique as a function of depth profiling. As the Br atom is at the top of the layer, its XPS signal is less attenuated compared with the C1s photoelectron signal. This attenuation of photoelectron as a function of overlayer distance is well known in XPS and greatly depends on packing density as well as overlayer orientation.

Detailed curve fitting (Gaussian-Lorentzian sum functions using XPS Peak software, version 4.1) of the Br3d XPS spectrum of wafer C shows that the experimental data (black line) can be deconvoluted into the two characteristic peaks ($3d_{5/2}$ and $3d_{3/2}$, pink and blue lines, respectively) for Br that are 1.05 eV apart (Figure 6b), consistent with only one type of Br. In contrast, curve-fitting analysis performed for the C1s XPS spectrum of wafer C shows that the experimental data (black line) obtained for C1s is actually a composite of two peaks (the aquamarine and blue lines, Figure 6a). The blue line is the major component of the experimental data and matched the assigned value for hydrocarbon C1s. The aquamarine line is a minor component of the experimental data and may be due to either oxidized carbon impurities on the sample surface or C atoms next to a highly electronegative Br atom.

Conclusion

In conclusion, 4-bromo-4'-vinylbiphenyl and 4-(*p*-bromo ethynylphenyl)styrene was successfully synthesized. In combination with 4-bromostyrene, these molecules have been used to form organic layers on HPS surfaces via UV-irradiation. The data indicated that only the alkene-substituted end of these molecules reacts, leaving the Br substituent exposed, as verified by XPS. Thus, the method used in this study may serve as a promising approach to preparing organic overlayers on silicon surfaces that can eventually be modified further.

Future work must verify the thickness of the layer as well as the packing density and orientation of the attached styrenic molecules. It may involve the use of the atomic force microscopy (AFM) as well as x-ray standing wave and x-ray reflectivity measurements to verify the monolayer nature of these organic layers. Furthermore, the methodology used in this study may be extended to the creation of fully conjugated organic monolayers on silicon surface via the reaction of HPS with acetylenic analogs of our styrene derivatives (Figure 7). Lastly, by functionalizing the surface-exposed Br substituent of the monolayers with biological molecules, a new form of biological sensing can be developed.

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