Chapter 4

Formation of Covalently Attached Polymer Overlayers on Si(111) Surfaces Using Ring-Opening Metathesis Polymerization Methods

This work was done in collaboration with Agnes Juang in the Lewis group and has previously appeared as: Juang, A.; Scherman, O. A.; Grubbs, R. H.; Lewis, N. S. *Langmuir* **2001**, *17*, 1321–1323.

4.1 Abstract

We describe a method for growing uniform, covalently attached polymer onto crystalline Si(111) surfaces. H-terminated Si was first chlorinated, and the surface-bound chlorine was then replaced by a terminal olefin using a Grignard reaction. A ruthenium ring-opening metathesis polymerization catalyst was then crossed onto the terminal olefin, and the resulting surface was subsequently immersed into a solution of monomer to produce the desired surface-attached polymer. The method provides a direct linkage between the polymer and the Si without the presence of an electrically-defective oxide layer. Growth of the polymeric layer could be controlled by varying the concentration of monomer in solution, and polynorbornene films between 0.9 and 5500 nm in thickness were produced through the use of 0.01 to 2.44 M solutions of norbornene.

4.2 Introduction

The fabrication of conducting and/or nonconducting organic overlayers on crystalline Si surfaces is of interest for inhibition of surface corrosion processes,[1] for providing routes to chemical control over the electrical properties of Schottky barrier-like structures,[2] for enabling novel lithographic strategies that utilize contact printing and photopatterning,[3–5] for producing novel metal-insulator-semiconductor devices,[6] and for controlling the electrical recombination properties of Si surfaces,[7, 8] amongst other applications. To obtain acceptable electrical device properties, many of these applications require direct functionalization of the Si surface in a fashion that does not introduce significant densities of interfacial electronic defect levels. The presence of a native oxide on Si is largely unacceptable for such purposes because the resulting Si/Si oxide interface is often highly electrically defective.[9, 10] In addition, the oxide acts as a tunneling barrier for charge carriers and the uniformity of this barrier is difficult to control at the molecular level. Thermally-grown silicon oxides generally contain fixed positive charge,[9, 11–13] which also limits the types of electrical device behavior that can be obtained from such interfaces.

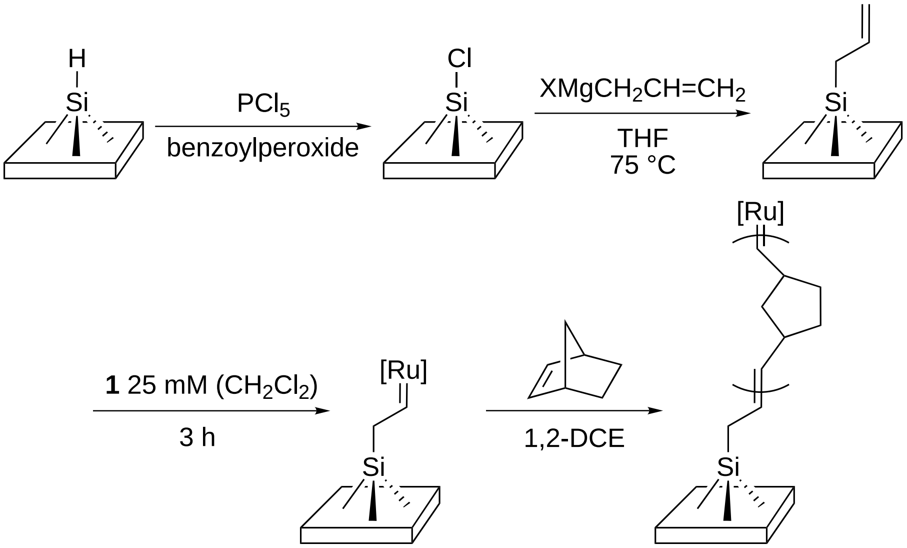
It would therefore be desirable to form electrically conductive or nonconductive barrier layers of controlled thickness on Si without relying on reactions that utilize functionality arising from native and/or thermally-grown overlayers of Si oxides. Crystalline Si has recently been functionalized using a variety of approaches;[14–28] notably, alkylation of crystalline, (111)-oriented Si using a two-step chlorination/alkylation procedure can produce functionalized surfaces that have a very low surface recombination velocity, <50 cm s^{-1}, and this low defect density of < 1 active electrical surface site per 50,000 surface atoms persists in ambient atmospheric conditions.[8] We describe herein the extension of this chemistry, combined with ring-opening metathesis polymerization (ROMP) methods, to produce organic overlayers that are covalently attached to Si(111) surfaces and that provide molecular-level control over the thickness and electronic properties of the resulting Si/polymer contacts.

4.3 Results and Discussion

Scheme 4.1 depicts our methodology (i) an alkene linker of variable length is coupled to a chlorinated Si surface using a Grignard reaction; (ii) an olefin cross-metathesis reaction is used to obtain a surface-bound ruthenium ROMP catalyst, and (iii) a monomer is added to effect growth of polymer onto the surface.

To implement this approach, a (111)-oriented crystalline n-type Si substrate 7 mm x 7 mm in dimensions was first etched in 49% buffered HF(aq) for 30 s and then for 15 min in 40% NH_4F(aq).[29] The resulting H-terminated Si surface was then chlorinated by exposure to saturated PCl_5 in chlorobenzene for 45 min at 90–100 °C, with a trace of benzoyl peroxide added to serve as a radical initiator.[30, 31] This chloride-capped Si surface[32] was then exposed to allylmagnesium chloride for 14–16 hr at 75 °C in tetrahydrofuran (THF).[32] A ruthenium olefin metathesis catalyst $(Cy_3P)_2Cl_2Ru{=}CHPh$ (Cy=cyclohexyl), (**1**),[33, 34] was then reacted with the olefin-modified Si surface by immersing the Si for 3 hr into a 25 mM solution of **1** in CH_2Cl_2. The substrate was then rinsed several times with CH_2Cl_2 to remove any non-bound

Scheme 4.1: Si(111) surface modification procedure.



catalyst. Exposure of the surface-bound catalyst to a 0.01–2.44 M solution of the norbornene monomer, **2**, for 30 min in 1,2-dichloroethane resulted in the growth of a polymeric film on the n-Si(111) surface. The resulting films were then repeatedly washed with CH_2Cl_2 and characterized as appropriate by X-ray photoelectron (XP) spectroscopy, ellipsometry, profilometry, and scanning electron microscopy (SEM).

Figure 4.1 displays the XP spectra obtained at each step of the surface modification process. The chlorination was verified by the presence of Cl 2s and Cl 2p peaks in the XPS survey scan (Figure 4.1d).[32] Attachment of the alkene carbon linker was confirmed by the disappearance of the Cl peaks and the concomitant increase in magnitude of the C 1s peak in the XP survey spectrum (Figure 4.1c).[35] For thin polymer films, growth of polymer was evidenced by the disappearance of the Si signals and the formation of an overlayer that only displayed C peaks in the XP survey scan (Figure 4.1a) whereas thicker polymer films produced no significant XPS signals, as expected if an electrically insulating organic overlayer had been formed on the surface.

Additional experiments were performed to establish that (i) the polymerization of **2** was directly initiated by **1**, and (ii) the resulting polymer film was attached covalently to the Si surface. When an olefin-terminated alkylated Si substrate was exposed to a solution of **2**, no polymer was observed by XPS. In addition, when a H-

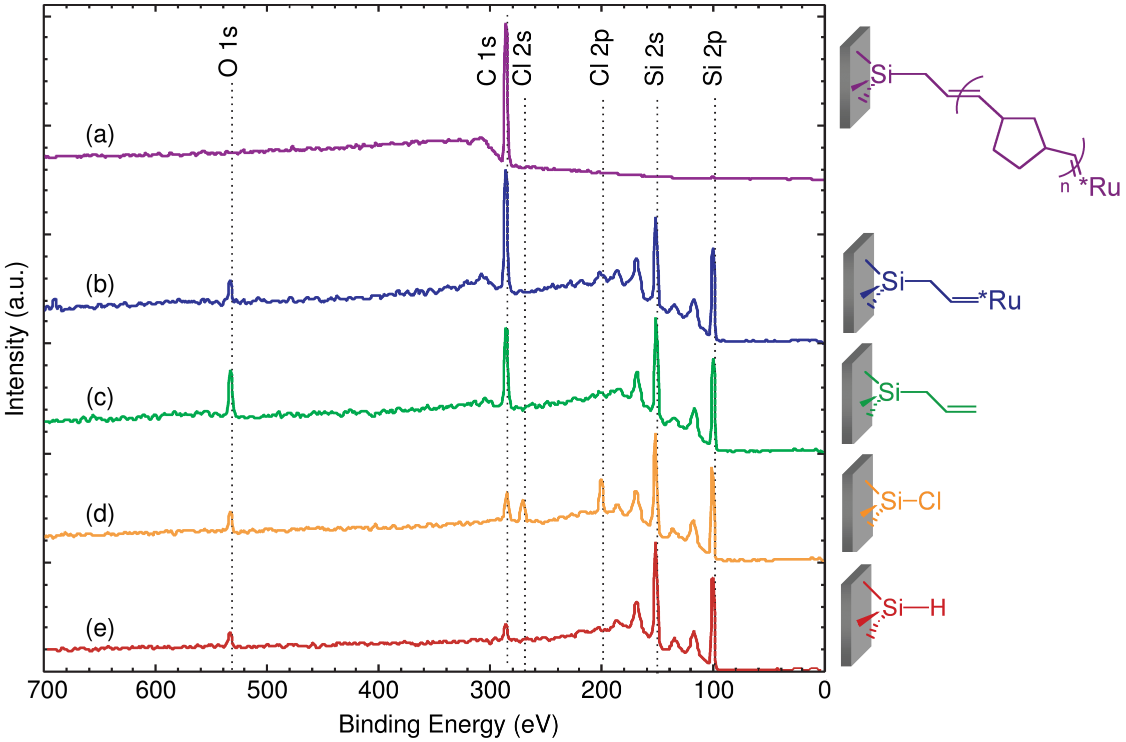


Figure 4.1: XPS survey scans. (a) covalently attached polynorbornene on Si, (b) allyl-terminated Si after immersing in a solution of **1** for 3 h, (c) allyl-terminated Si, (d) Cl-terminated Si, and (e) H-terminated Si. Spectra in a–d are normalized relative to the intensity of the Si 2p peak.

terminated Si surface was exposed to a solution of **2**, no polymer formed and the XPS signals showed only Si and a very small amount of adventitious C and O. Exposure of a H-terminated Si surface to a solution of **1** followed by exposure to a solution of **2** produced a polymer that did not persist on the Si surface after washing with CH_2Cl_2. These wet chemical experiments imply that the above technique did in fact produce covalently attached polymeric films on the Si surface, and the polymerization could not occur without the Ru initiators.

Figure 4.2 displays a SEM image of the cross section of a sample (obtained after immersion of a **1**-treated, allyl-terminated Si sample into a 2.44 M solution of norbornene in 1,2-dichloroethane for 30 min) at 1500x magnification. The SEM images indicate that the wafers were indeed covered entirely by polynorbornene. The estimated thickness of the polymer film from SEM images of two samples at 1500x magnification is 5.6±0.06 μm, which agrees with the thickness of 5.5 μm measured

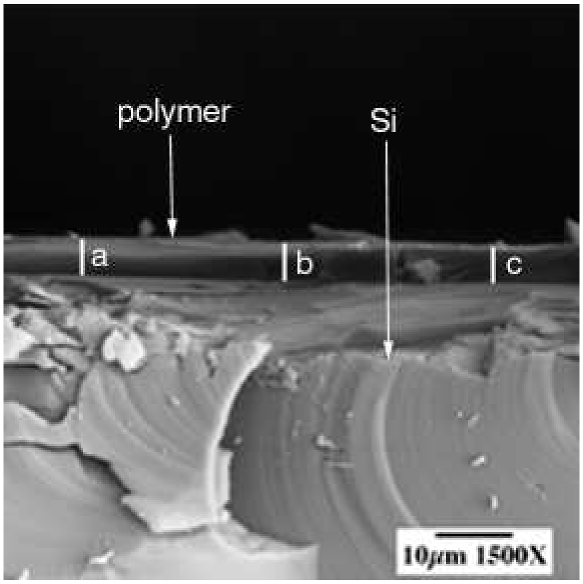


Figure 4.2: SEM of polynorbornene-modified Si(111) surface. A cross-sectional SEM image of a polynorbornene-covered Si surface at 1500x magnification. The polymer film covered the entire Si substrate, and the estimated film thickness at points a, b, and c from the SEM image are 5.0, 5.5, and 5.4 μm, respectively. These values are in good agreement with the mean polymer thickness of 5.5 μm that was determined for this same sample using profilometry.

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Because ROMP initiated by **1** is a controlled polymerization process,[34, 36] different film thicknesses could be obtained by varying the concentration of **2** in 1,2-dichloroethane solutions. Table 4.1 summarizes the thicknesses of several polymer films produced at a fixed reaction time (30 min) in response to variation in the concentration of monomer in the solution. The standard deviation in the ellipsometrically derived thickness measured at six different spots for each sample was usually $< \pm 10\%$ of the mean thickness value, indicating that the polymer film covered the entire Si substrate. Consistently, the SEM image of Figure 4.2 yielded a film thickness of 5.3±0.2 μm over a distance of 75 μm.

The method would appear to be general in that a wide range of monomers can be polymerized with **1**[36, 38–40] and could be used to form overlayers of controlled thickness on Si surfaces. When the first polymer layer is electrically insulating (as in the present case), this should allow formation of metal-insulator-semiconductor

Table 4.1: Dependence of the polymer film thickness on the concentration of norbornene in solution.

Monomer Concentration (M)	Thickness[a] (Å)
0.01	9±1
0.09	120±14
0.18	420±140
0.27	1280±660

[a] Each thickness value is an average of measurements on at least four samples, with six different locations measured on each sample.[37]

structures or of capacitors of controlled thickness, whereas when the first polymer is metallic or semiconducting in nature (e.g., when cyclooctatetraenes, phenylenevinylenes, etc., are used as feedstocks),[41] the process should provide a route to formation of semiconductor/metal or semiconductor heterojunction structures. Langmuir-Blodgett techniques[42] have been used to synthesize organic thin films with controlled structure and composition; however, the fragility of the resulting films represents a major obstacle to practical implementation. More robust films have been obtained using polymers with functionalities appropriate for covalent attachment to surfaces.[43] The significant improvement in physical properties, however, generally is accompanied by a loss of control over the order and composition of the overlayer. Weck *et al.* reported the ROMP of substituted norbornenes from a modified gold surface, but only small amounts of polymer were formed.[40] The procedure described herein is analogous to that reported recently by Kim *et al.*, who used ROMP to produce substituted norbornenes from a self-assembled monolayer of 5-(bicycloheptenyl)trichlorosilane formed on a silicon wafer bearing a native oxide (Si/SiO_2),[39] followed by opening of the olefin and exchange with the catalyst. Our approach is complementary to this work in that the present method allows for the formation of covalently attached interfacial polymeric layers in situations in which the presence of an intervening Si oxide layer is undesirable.

4.4 Conclusions

In conclusion, we have demonstrated the growth of polymer films that are covalently attached to Si surfaces via a Si-C linkage. The thickness of the linker unit can be controlled at the molecular level, and the thickness of the polymer can be independently controlled by varying the concentration of monomer, so that polymer thicknesses between 0.9 and 5500 nm can be obtained.

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