

Building Conjugated Organic Structures on Si(111) Surfaces via  
Microwave-Assisted Sonogashira CouplingJui-Ching Lin,<sup>†,||</sup> Jun-Hyun Kim,<sup>‡,||</sup> Joshua A. Kellar,<sup>†</sup> Mark C. Hersam,<sup>†,‡</sup>  
SonBinh T. Nguyen,<sup>\*,‡</sup> and Michael J. Bedzyk<sup>\*,†,§</sup><sup>†</sup>Department of Materials Science and Engineering, <sup>‡</sup>Department of Chemistry, and <sup>§</sup>Department of Physics and Astronomy, Northwestern University, Evanston, Illinois 60208. <sup>||</sup> These authors contributed equally to this work.

Received September 21, 2009. Revised Manuscript Received February 1, 2010

A novel step-by-step method employing microwave-assisted Sonogashira coupling is developed to grow fully conjugated organosilicon structures. As the first case study, *p*-(4-bromophenyl)acetylene is covalently conjugated to a *p*-(4-iodophenyl)acetylene-derived monolayer on a Si(111) surface. By bridging the two aromatic rings with C≡C, the pregrown monolayer is structurally extended outward from the Si surface, forming a fully conjugated (*p*-(4-bromophenylethynyl)phenyl)vinylene film. The film growth process, which reaches 90% yield after 2 h, is characterized thoroughly at each step by using X-ray reflectivity (XRR), X-ray standing waves (XSW), and X-ray fluorescence (XRF). The high yield and short reaction time offered by microwave-assisted surface Sonogashira coupling chemistry make it a promising strategy for functionalizing Si surfaces.

## Introduction

The integration of silicon with functionalized organic molecules is of great interest in the development of chemical and biological sensors.<sup>1–3</sup> In particular, coupling sp<sup>2</sup>- or sp-hybridized organic molecules to Si surfaces should facilitate interaction between the external environment and silicon-based electronics through delocalized electron transport over the C π to Si σ conjugation bridge.<sup>4</sup> To this end, we recently demonstrated that aryl-substituted acetylenes can be used to functionalize a Si(111) surface under mild UV irradiation, forming a fully conjugated monolayer structure with sp<sup>2</sup>-conjugated moieties directly connected to surface Si atoms.<sup>5</sup> When *p*-(4-bromophenyl)acetylene (BPA) is used as the modifier in this chemistry, the halogen is preserved at the top of the monolayer, in contrast to the previous deployment of monolayers based on undec-10-enoic acid 2-bromo-ethyl ester,<sup>6</sup> providing a ready handle for sequential substitution chemistry through Pd-based couplings, such as the Sonogashira reaction.<sup>7,8</sup>

Although Sonogashira coupling has been widely used in solution-phase chemistry<sup>8</sup> to extend the conjugated structure of aromatic halides through C≡C bridges, its application to the solid

phase has been rare.<sup>9,10</sup> Herein, we report a detailed stepwise study of a microwave-assisted Sonogashira coupling to a Si(111) surface possessing an sp<sup>2</sup>-conjugated monolayer, resulting in a more extended conjugation structure. Specifically, *p*-(4-bromophenyl)acetylene (BPA) is coupled to a *p*-(4-iodophenyl)acetylene (IPA)-derived monolayer on Si(111) to form a (*p*-(4-bromophenylethynyl)phenyl)vinylene layer on a Si surface (Scheme 1). The increased thickness of the Si-supported molecular layer can be clearly observed by X-ray reflectivity (XRR) analysis, confirming the successful conjugation. The extent of coupling is directly assessed via X-ray standing wave (XSW) and X-ray fluorescence (XRF) measurements of the iodine and bromine contents of the surface. Because alkyne handles can be readily incorporated into a wide range of bioactive compounds,<sup>11,12</sup> the present Sonogashira coupling chemistry may provide a facile strategy for coupling Si-based electronic devices to a wide range of biomedical applications.

In a typical Sonogashira reaction, the sp–sp<sup>2</sup> coupling between the aryl-halide and alkynes usually takes place in the presence of a base.<sup>8</sup> Conventional Sonogashira coupling often requires an extended reaction time<sup>13,14</sup> or high reaction temperature.<sup>13,15</sup> In contrast, microwave-assisted Sonogashira coupling can proceed more rapidly while affording higher yields that are beneficial in solid-phase reactions.<sup>8,16</sup> As such, we employed microwave-assisted conditions in our study to accelerate the reaction rate and promote the coupling yield between the IPA-derived film on Si(111) (IPA/Si(111), sample S1) and BPA (Scheme 1). For comparison, we also separately prepared a (*p*-(4-bromophenylethynyl)phenyl)vinylene monolayer film on a Si(111) surface

\*Corresponding authors. E-mail: stn@northwestern.edu, bedzyk@northwestern.edu.

(1) Wagner, P.; Nock, S.; Spudich, J. A.; Volkmuth, W. D.; Chu, S.; Cicero, R. L.; Wade, C. P.; Linford, M. R.; Chidsey, C. E. D. *J. Struct. Biol.* **1997**, *119*, 189–201.

(2) Perring, M.; Dutta, S.; Arafat, S.; Mitchell, M.; Kenis, P. J. A.; Bowden, N. B. *Langmuir* **2005**, *21*, 10537–10544.

(3) Strother, T.; Cai, W.; Zhao, X.; Hamers, R. J.; Smith, L. M. *J. Am. Chem. Soc.* **2000**, *122*, 1205–1209.

(4) Sakurai, H. *Pure Appl. Chem.* **1987**, *59*, 1637–1646.

(5) Kellar, J. A.; Lin, J.-C.; Kim, J.-H.; Yoder, N. L.; Bevan, K. H.; Stokes, G. Y.; Geiger, F.; Nguyen, S. T.; Bedzyk, M. J.; Hersam, M. C. *J. Phys. Chem. C* **2009**, *2919*–2927.

(6) Jin, H.; Kinsler, C. R.; Bertin, P. A.; Kramer, D. E.; Libera, J. A.; Hersam, M. C.; Nguyen, S. T.; Bedzyk, M. J. *Langmuir* **2004**, *20*, 6252–6258.

(7) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467–4470.

(8) Chinchilla, R.; Najera, C. *Chem. Rev.* **2007**, *107*, 874–922.

(9) Qu, M.; Zhang, Y.; He, J.; Cao, X.; Zhang, J. *Appl. Surf. Sci.* **2008**, *255*, 2608–2612.

(10) Testero, S. A.; Mata, E. G. *J. Comb. Chem.* **2008**, *10*, 487–497.

(11) Bohlmann, F.; Burkhardt, T.; Zdero, C. *Naturally Occurring Acetylenes*; Academic Press: London, 1973.

(12) Lam, J.; Breteler, H.; Arnason, T.; Hansen, L. *Chemistry and Biology of Naturally Occurring Acetylenes and Related Compounds*; Elsevier Science Ltd: New York, 1989.

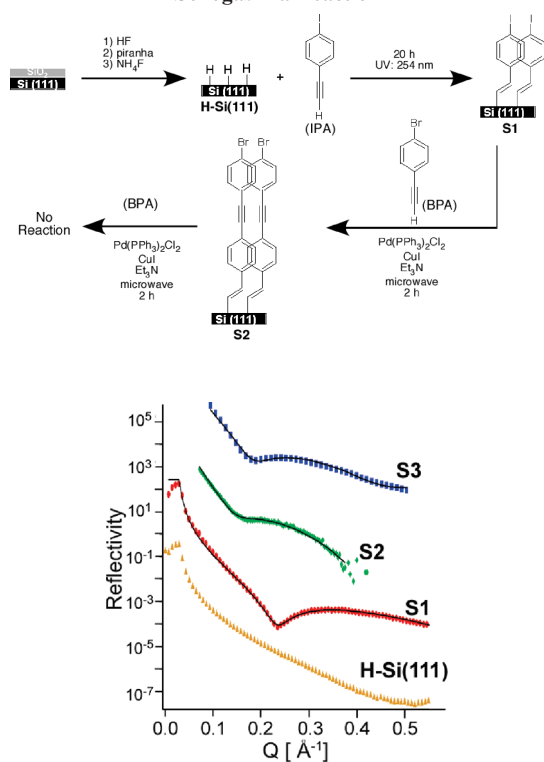
(13) Thakur, K. G.; Jaseer, E. A.; Naidu, A. B.; Sekar, G. *Tetrahedron Lett.* **2009**, *50*, 2865–2869.

(14) Eckhardt, M.; Fu, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 13642–13643.

(15) Stein, A. L.; Alves, D.; da Rocha, J. T.; Nogueira, C. W.; Zeni, G. *Org. Lett.* **2008**, *10*, 4983–4986.

(16) Erdelyi, M.; Gogoll, A. *J. Org. Chem.* **2003**, *68*, 6431–6434.

**Scheme 1. *p*-(4-Iodophenyl)acetylene-Based Monolayer First Grown on a H-Passivated Si(111) Surface and Subsequently Coupled to *p*-(4-Bromophenyl)acetylene via a Microwave-Assisted Sonogashira Reaction**



**Figure 1.** XRR data for the respective H-Si(111) (S1), [IPA/Si(111) + BPA] Sonogashira-prepared (S2), and standard BPPA/Si(111) (S3) thin films (triangles, circles, diamonds, and squares, respectively). The solid lines are theoretical fits based on Parratt's recursion method<sup>19</sup> using a two-layer/Si model (i.e., halogen and hydrocarbon layers). The structural parameters from the fits are listed in Table 1. For purposes of clarity, S1, S2, and S3 are vertically offset by  $10^3$ ,  $10^6$ , and  $10^9$ , respectively.

(BPPA/Si(111), sample S3) via the photoinduced hydrosilylation of (*p*-4-bromophenylethynyl)phenylacetylene (BPPA) by H-passivated Si(111) (H-Si(111)).<sup>17</sup> This S3 sample, which is prepared in only a single step, has the same monolayer composition as the S2 Sonogashira-prepared sample and will therefore serve as a standard for evaluating our Sonogashira-coupling chemistry method.

### Experimental Section

The details of the sample preparation and experimental measurements are provided in the Supporting Information.

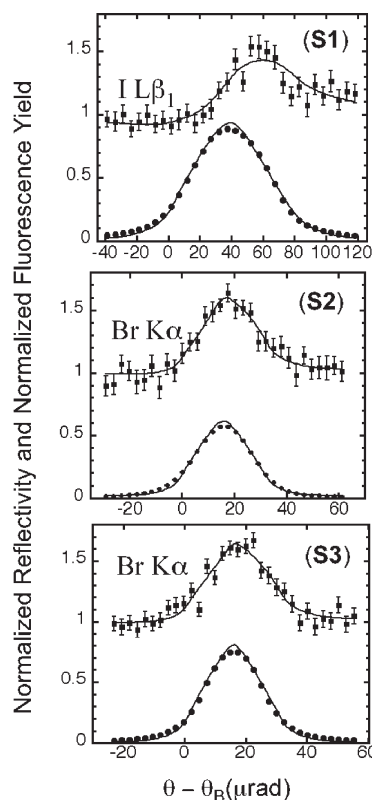
### Results and Discussion

Figure 1 shows the XRR analysis of the film after each step in our Sonogashira-based organic film growth process, as well as that of the standard S3. In contrast to the smooth Fresnel-like decay of the H-Si(111) interface, the IPA/Si(111) (S1) and the Sonogashira-prepared (S2) films show clear interference thickness oscillations. In addition, the antireflection dip in the Sonogashira-prepared sample is shifted to a lower value ( $Q = 0.17 \text{ \AA}^{-1}$ ) compared to S1 ( $Q = 0.23 \text{ \AA}^{-1}$ ). Because the antireflection dip in the XRR measurement is sensitive to the thickness of the organic

**Table 1. XRR Two-Layer/Si Model-Determined Relative Electron Density ( $\rho = \rho_{\text{layer}}/\rho_{\text{Si}}$ ), Thickness ( $t$ ), and Interfacial Roughness ( $\sigma$ ) of Each Layer<sup>a</sup>**

	$t_3$ (Å)	$\rho_3$	$t_2$ (Å)	$\rho_2$	$\sigma_{1,2}$ (Å)	$\sigma_{2,3}$ (Å)	$\sigma_{3,4}$ (Å)
S1	8.6	0.5	0.7	2.1	3.2	1.8	2.4
S2	14.4	0.6	0.3	2.2	6.7	5.1	3.7
S3	14.1	0.7	0.9	2.5	4.0	2.5	2.0

<sup>a</sup> Layers 1–4 are air, halogen, hydrocarbon, and Si, respectively.



**Figure 2.** 111 XSW analyses showing the experimental and theoretical angular dependences for the X-ray reflectivity and the X-ray fluorescence for the IPA/Si(111) film (S1), the [IPA/Si(111) + BPA] Sonogashira-prepared film (S2), and the standard BPPA/Si(111) film (S3).

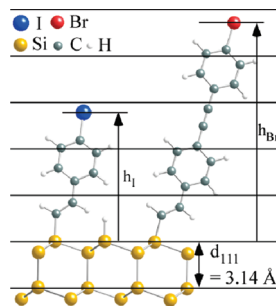
film on Si and a smaller  $Q$  for the dip corresponds to a thicker film,<sup>18</sup> the initial organic layer in S1 has clearly been extended outward from the Si surface in S2 (i.e., after the reaction). The observation that the antireflection dips occur at the same  $Q$  for samples S2 and S3 serves to confirm the expected final BPPA-derived (*p*-4-bromophenylethynyl)-phenylvinylene monolayer structure for S2 as shown in Scheme 1. Referring to the XRR analysis<sup>19</sup> in Table 1, monolayers S2 and S3 have equivalent thicknesses (defined as the height of the center of the halogen layer,  $t_3 + 1/2t_2 = 14.6 \text{ \AA}$ ), as would be expected for isostructural films.

Under our surface Sonogashira coupling scheme (Scheme 1), it is possible that the Sonogashira-formed (*p*-4-bromophenylethynyl)phenylvinylene monolayer could have undergone further coupling with BPA. In addition, BPA could have undergone self-coupling in solution to generate BPPA. Given that the Sonogashira couplings between phenylacetylene and iodo-aromatics

(17) Kim, J.-H.; Lin, J.-C.; Kellar, J. A.; Hersam, M. C.; Bedzyk, M. J.; Nguyen, S. T. To be submitted for publication.

(18) Tolán, M. *X-ray Scattering from Soft-Matter Thin Films: Materials Science and Basic Research*; Springer-Verlag: New York, 1999.

(19) Nelson, A. J. *Appl. Crystallogr.* **2006**, *39*, 273–276.



**Figure 3.** Ball-and-stick models for IPA-derived (left) and BPPA-derived (right) covalent monolayer on Si(111) surfaces. The XSW-determined heights of iodide ( $h_I$ ) and bromide ( $h_{Br}$ ) are measured with respect to the Si substrate  $d_{111}$  spacing.  $P_{111} = h/d_{111}$  modulo-1.

are much faster than the analogous reactions with bromoaromatics, the coupling between BPA and the iodine-terminated monolayer on **S1** should occur in a more facile fashion over both of the aforementioned possibilities during our short reaction time. Further support for this hypothesis was provided by our observation that BPA did not couple to a Br-styrene-derived monolayer on Si(111) under identical microwave-assisted Sonogashira coupling conditions and BPPA was not found to be a side product in the synthesis of **S2** (Supporting Information, SI). These results suggest that the selective patterning of organic molecules on a Si(111) surface via surface Sonogashira coupling may be possible via the judicious deployment of organic monolayers with different halide termination.

In contrast to XRR, which measures the “averaged electron density” profile for the organic/Si interface structures,<sup>18</sup> the 111 XSW analysis, with the XRF modulation observed while scanning through the Si(111) Bragg reflection (Figure 2), directly measures the spatial distribution of the fluorescence marker atoms (Br and/or I) with respect to the lattice of the single-crystal substrate (i.e.,  $d_{111}$  spacing, Figure 3). As a result, XSW is element-specific and has subangstrom resolution.<sup>20–23</sup> The XSW results for the IPA/Si(111) starting film (**S1**), the Sonogashira-prepared film (**S2**), and the standard BPPA/Si(111) film (**S3**) are shown in Figure 2 and Table 2. The differences between the Br  $K\alpha$  (**S2**) and I  $L\beta_1$  (**S1**) XSW modulations indicate the variance in the vertical distributions of the halogen atoms before and after the Sonogashira reaction. The coherent fraction  $f_{111}$  and coherent position  $P_{111}$  in the XSW analysis measures the distribution width of the XRF-selected fluorescence species and the location of the distribution center, respectively.<sup>24,25</sup> The smaller coherent fraction  $f_{111}$  from **S2** compared to **S1** (Table 2) suggests a broader vertical distribution of Br atoms in Sonogashira-prepared sample **S2** than for I atoms in IPA/Si(111) monolayer **S1**. This is consistent with the fact that the Br atoms in the former are set further away from the Si surface than the I atoms in the latter by an extended spacer group after Sonogashira coupling (Figure 3).

(20) Bedzyk, M. J.; Cheng, L. W. *Rev. Mineral. Geochem.* **2002**, *49*, 221–266.

(21) Zegenhagen, J. *Surf. Sci. Rep.* **1993**, *18*, 199–271.

(22) Golovchenko, J. A.; Patel, J. R.; Kaplan, D. R.; Cowan, P. L.; Bedzyk, M. J. *Phys. Rev. Lett.* **1982**, *49*, 560–563.

(23) Batterman, B. W. *Phys. Rev.* **1964**, *133*, A759.

(24) Lin, J.-C.; Kellar, J. A.; Kim, J.-H.; Yoder, N. L.; Bevan, K. H.; Nguyen, S. T.; Hersam, M. C.; Bedzyk, M. J. *Eur. Phys. J. Spec. Top.* **2009**, *168*, 33–39.

(25) Basu, R.; Lin, J.-C.; Kim, C.-Y.; Schmitz, M. J.; Yoder, N. L.; Kellar, J. A.; Bedzyk, M. J.; Hersam, M. C. *Langmuir* **2007**, *23*, 1905–1911.

**Table 2.** XSW and XRF Results for the IPA/Si(111) Film (**S1**), the Sonogashira-Prepared Film (**S2**), and the Standard BPPA/Si(111) Film (**S3**)

	iodide			bromide		
	Cov (ML)	$f_{111}$	$P_{111}$	Cov (ML)	$f_{111}$	$P_{111}$
<b>S1</b>	0.15(1)	0.44(5)	0.77(3)			
<b>S2</b>				0.14(3)	0.19(4)	0.73(3)
<b>S3</b>				0.22(2)	0.17(4)	0.70(2)

The agreement in the XSW-obtained  $f_{111}$  and  $P_{111}$  values for Br in **S2** and **S3** is consistent with the previously discussed XRR results, which contained an identical film thickness (and hence molecular structure) on the Si surface regardless of the growth method. In conjunction with the longer-length-scale XRR measurement,<sup>26</sup> the XSW analysis yields the height of Br in Sonogashira-prepared sample **S2** to be  $h_{Br} = [4 + P_{111}]d_{111} = 14.8 \text{ \AA}$ . For comparison, the height of the I atom in sample **S1** before the coupling reaction is  $h_I = [2 + P_{111}]d_{111} = 8.7 \text{ \AA}$  (Figure 3). For **S3**,  $h_{Br} = 14.7 \text{ \AA}$ .

In our surface Sonogashira coupling scheme (Scheme 1), the terminal iodide from the IPA/Si(111) monolayer in sample **S1** is replaced by a BPA group in creating sample **S2**. Hence, the coupling reaction yield can be determined by measuring both the loss in iodide coverage and the gain in bromide coverage. The XRF-calibrated iodide and bromide coverages (Table 2) show an iodide loss equivalent to a bromide gain of 0.14 monolayer (ML) after microwave-assisted Sonogashira coupling. Compared to the initial 0.15 ML of iodide, this amounts to  $\sim 90\%$  yield for the reaction.

## Conclusions

We have demonstrated that a microwave-assisted surface Sonogashira coupling reaction can be employed to construct extended conjugated organic structures on Si(111) surfaces. In this manner, halide-terminated alkenyl monolayers on silicon can be systematically functionalized with a wide range of substituted alkynes, providing an entry point for integrating biosensing with Si-based electronics.

**Acknowledgment.** This work was supported by the Nanoscale Science and Engineering Initiative of the National Science Foundation (award numbers EEC-0647560 and ECS-0506802) and the Office of Naval Research Young Investigator Award (award numbers N00014-05-1-0563 and N00014-09-1-0180). We thank the DND-CAT and XOR/UNI-CAT staffs and Jerrold Carsello of the NU X-ray laboratory for technical assistance. Use of the APS at Argonne National Laboratory was supported by the DOE/BES under contract no. DE-AC02-06CH11357. This work made use of NU Central Facilities supported by the MRSEC through NSF contract no. DMR-0520513.

**Supporting Information Available:** Details of the synthesis of the reagents, procedures for the synthesis of the Si(111)-supported monolayers, procedure for the microwave-assisted Sonogashira chemistry, and analyses of the XRR, XSW, and XRF data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(26) As described in refs 5, 24, and 25, the film thickness determined by XRR analysis can be used to remove the modulo-d ambiguity in the XSW height determination.