

## Improved Polypyrrole/Silicon Junctions by Surface Modification of Hydrogen-Terminated Silicon Using Organolithium Reagents

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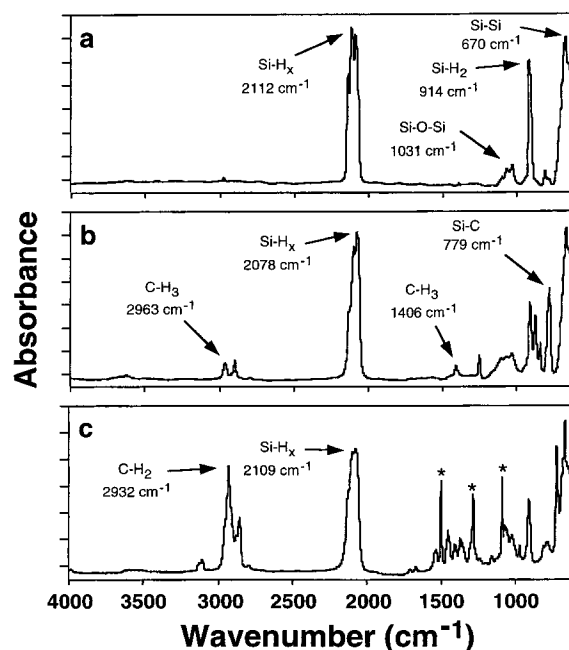
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Conducting polymers offer an attractive tailorability for use in various electronic and photonic applications.<sup>1</sup> The integration of these materials with inorganic semiconductors is challenged by the need to intimately contact the organic and inorganic phases for efficient electrical and optical coupling.<sup>1–5</sup> In the formation of conducting polymer/semiconductor junctions, the polymer is often deposited on the semiconductor by spin-coating or electrochemical polymerization. The resulting polymer/semiconductor junctions are generally beset by poor interfacial interactions that diminish their physical and electrical performance.<sup>1–5</sup> Simon et al.<sup>6</sup> reported the use of a pyrrole-terminated alkylsiloxane monolayer on silicon to provide a covalent link between an inorganic semiconductor and an electropolymerized organic polymer.<sup>7</sup> The resulting polypyrrole/silicon junction exhibited improved adhesion and offered protection to n-type silicon against photoanodic decomposition. An oxide surface was required for formation of the siloxane monolayer, and precluded investigation into the electrical properties of these polypyrrole/silicon contacts. The formation of conducting polymer films directly onto silicon without an intervening layer of oxide would be highly desirable for both fundamental studies of such hybrid polymer/silicon junctions and their practical use.

In this paper, we report the direct covalent junction between a conductive polypyrrole film and silicon using a reaction that attaches pyrrole units directly to the silicon surface. In particular, the reaction between an organolithium reagent and a hydrogen-terminated silicon surface allows direct attachment of pyrrole moieties to the silicon surface and does not require the presence of an intervening oxide layer. The use of an organolithium reagent<sup>8</sup> to modify hydrogen-terminated silicon proceeds on both porous and crystalline silicon substrates and produces films with higher coverages than those obtained by reaction with Grignard reagents.<sup>9</sup>

Figure 1a shows a diffuse-reflectance infrared spectrum for porous silicon that was formed by electrochemically etching Si(100) in HF acid/ethanol. The spectrum exhibits peaks for Si–H<sub>x</sub>, Si–O, and Si–Si stretching at 2117, 1067, and 670 cm<sup>-1</sup>,



**Figure 1.** Diffuse reflectance infrared spectra for (a) native porous silicon and after derivatization at room temperature for 2 h with (b) methylLi and (c) 5-(*N*-pyrrolyl)pentylLi and quenched with HCl in ether. The peaks with asterisks (\*) in (c) are for the pyrrole ring.

respectively, and Si–H<sub>2</sub> bending at 914 cm<sup>-1</sup>. After exposure to 1.6 M CH<sub>3</sub>Li in THF at room temperature for 2 h and a subsequent quench by addition of 1 M HCl in ether, the porous silicon exhibits peaks for methyl stretching at 2963 and 2897 cm<sup>-1</sup>, methyl bending at 1406 and 1248 cm<sup>-1</sup>, and Si–C stretching at 779 cm<sup>-1</sup> (Figure 1b).<sup>10</sup> The presence of the Si–C absorption reveals that CH<sub>3</sub>Li forms a covalent bond to the silicon surface. When porous silicon is sequentially treated with CH<sub>3</sub>Li and quenched with CH<sub>3</sub>CO<sub>2</sub>D, its spectrum displays a peak at 1513 cm<sup>-1</sup> for Si–D stretching in addition to the peaks in Figure 1b; in contrast, we observed no Si–D peak when porous silicon was exposed only to CH<sub>3</sub>CO<sub>2</sub>D. As the general spectral changes mirror those for the reactions of porous silicon with Grignard reagents,<sup>9</sup> we suggest that the reaction with RLi to form Si–C attachments is likely to proceed similarly by breakage of surficial Si–Si bonds.

We observed related spectral changes for reactions of porous and crystalline silicon substrates with organolithium reagents such as butyl-, hexyl-, and phenylLi.<sup>11</sup> Derivatized samples exhibited no change in their IR spectra after exposure to ultrahigh vacuum, HF (aqueous) in ethanol, or sonication in toluene, further suggesting formation of a robust, covalent attachment to the silicon surface. The derivatization of these hydrogen-terminated silicon surfaces by organolithium reagents yielded a higher coverage of attached species than reactions using Grignard reagents (For a comparison of samples derivatized by hexylLi and hexylMgBr, see the Supporting Information). The higher coverages were suggested by IR spectroscopy, where the C–H<sub>x</sub> stretching intensity was greater for a sample modified by an organolithium reagent than by a corresponding Grignard reagent and likely reflected the more reactive nature of an organolithium reagent. The greater reactivity of an organolithium reagent was also evident by a more significant decrease in the Si–H<sub>x</sub> stretching intensity than after reaction with a Grignard reagent. This

(10) Chazalviel, J.-N.; Vieillard, C.; Warntjes, M.; Ozanam, F. *Proc. Electrochem. Soc.* **1995**, 95–25, 249–257.

(11) IR spectra for crystalline silicon were obtained by attenuated total reflection.

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(1) *Handbook of Conducting Polymers*; Skotheim, T. A., Ed; Marcel Dekker: New York, 1986; Vol 1.

(2) Lonergan, M. C. *Science* **1997**, 278, 2103–2106.

(3) Hoshino, K.; Tokutomi, K.; Iwata, Y.; Kokada, H. *J. Electrochem. Soc.* **1998**, 145, 711–720.

(4) Kokado, H.; Hosokawa, F.; Hoshino, K. *Jpn. J. Appl. Phys.* **1993**, 32, 189–194.

(5) Watanabe, A.; Murakami, S.; Mori, K.; Kashiwaba, Y. *Macromolecules* **1989**, 22, 4231–4235.

(6) Simon, R. A.; Ricco, A. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1982**, 104, 2031–2034.

(7) The improved formation of conducting polymers on gold using monomer-terminated thiol-based monolayers has been reported by: (a) Willcutt, R. J.; McCarley, R. L. *Langmuir* **1995**, 11, 296–301. (b) Sayre, C. N.; Collard, D. M. *Langmuir* **1995**, 11, 302–306. (c) Rubinstein, I.; Rishpon, J.; Sabatani, E.; Redondo, A.; Gottesfeld, S. *J. Am. Chem. Soc.* **1990**, 112, 6135–6136. (d) Kowalik, J.; Tolbert, L.; Ding, Y.; Bottomley, L. A. *Synth. Met.* **1993**, 55–57, 1171–1175.

(8) Song, J. H.; Sailor, M. J. *J. Am. Chem. Soc.* **1998**, 120, 2376–2381.

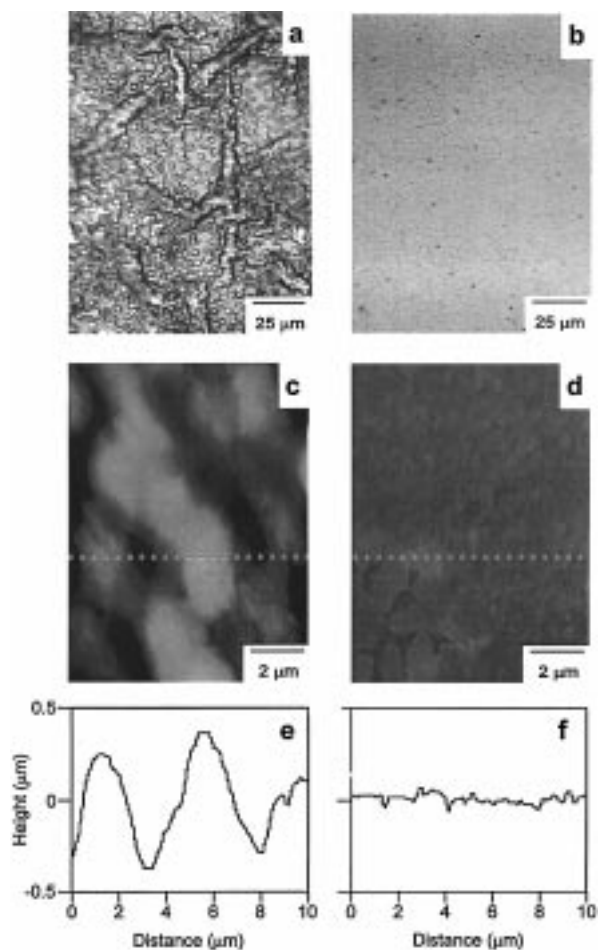
(9) Kim, N. Y.; Laibinis, P. E. *J. Am. Chem. Soc.* **1998**, 120, 4516–4517.

difference suggests that the organolithium reaction occurs with a greater degree of Si–Si bond cleavage than with Grignard reagents.

Using this strategy for modifying the silicon surface, we derivatized various H-terminated silicon samples with 5-(*N*-pyrrolyl)pentylLi. Figure 1c shows the IR spectrum for porous silicon after treatment with 0.2 M 5-(*N*-pyrrolyl)pentylLi in THF, as produced by reaction between 1-bromo-5-(*N*-pyrrolyl)-pentane<sup>7a</sup> and the lithium–naphthalene radical.<sup>12</sup> The peaks between 1100 and 3100  $\text{cm}^{-1}$  agree well with those for a 5-(*N*-pyrrolyl)pentyl species by comparison to the IR spectrum for neat 1-bromo-5-(*N*-pyrrolyl)-pentane (see Supporting Information). The modification of p-type Si(100) was supported similarly by IR and also by XPS where the samples displayed a new peak for nitrogen and increased peak intensity for carbon after derivatization (see Supporting Information). As the spectral region for Si(2p) showed no change in position or shape and the O(1s) signal exhibited only a slight increase after reaction, the organolithium reaction appears to proceed with no (or little) oxidation of the surface. By XPS, we estimated a surface coverage of  $\sim 60\%$  for the pyrrole film by comparing its N(1s) intensity to that for a SAM of HS-(CH<sub>2</sub>)<sub>10</sub>CONH<sub>2</sub> on gold.

Using both native and modified H-terminated Si(100) as electrodes, we electrochemically deposited polypyrrole films on their surfaces.<sup>13</sup> For galvanostatically controlled polymerizations, the deposition potentials exhibited less temporal variation for the modified silicon, suggesting a more uniform growth of the polymer.<sup>7c</sup> The polypyrrole film on H-terminated silicon was black and had a visibly rough texture, while the polymer on the modified silicon was dark blue and had a mirrorlike finish by eye. Figure 2 shows optical and AFM images for the polymers on these silicon surfaces. The differences in surface morphology are readily apparent, where the unmodified substrate (Figure 2a) shows a rougher surface than the modified one (Figure 2b). By AFM, the polymer on the modified surface was typically 7–10 times smoother than that on the native hydrogen-terminated surface.<sup>13</sup> The surface modification with 5-(*N*-pyrrolyl)pentylLi also improved the adhesion of polypyrrole to silicon. For example, on the native H-terminated silicon, the polymer often peeled from the surface upon rinsing with ethanol or drying under a stream of N<sub>2</sub> and could be completely removed in a single application of Scotch tape. In contrast, polypyrrole on the modified silicon was not removed by these conditions or the repeated application of tape. We could only remove the polymer film from silicon as fragments by scratching with a metal stylus.

We attribute the above morphological and adhesional differences in the polymer films to changes in the nucleation and growth on the two substrates.<sup>7</sup> The substrate modification provides organic sites on the silicon surface for polymer attachment that aid the electrodeposition process. This change to a more regular and uniform growth is supported by the greater constancy of the deposition potential during electrochemical polymerization onto the modified samples. We excluded the possibility that the difference was due simply to the alkyl chains of the 5-(*N*-pyrrolyl)pentyl film, as polypyrrole deposited onto silicon derivatized by CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>Li exhibited similar characteristics as on native H-terminated silicon.<sup>14</sup> We conclude that the incorporated pyrrole units on the silicon surface are responsible for the quality



**Figure 2.** Optical (a,b) and AFM (c,d) images for polypyrrole films<sup>13</sup> on native (a,c) and modified (b,d) hydrogen-terminated silicon. (e,f) cross-sectional views for the dashed line in (c) and (d), respectively.

of these conducting polymer thin films by providing a covalent link between the polymer and silicon. This procedure should be general for other silicon/conducting polymer junctions. Our present investigations are examining the current–voltage characteristics of these junctions on substrates of various dopant densities. By cyclic voltammetry, the junctions to both p- and n-type silicon exhibit rectification, with the junctions on the modified silicon exhibiting up to 100 times higher current densities in forward bias than those on the native H-terminated silicon (see Supporting Information). Presently, the presence of the pyrrole-containing film on the surface of silicon appears to improve the electrical properties of the polypyrrole/silicon junction by enhancing interfacial charge transfer between the two phases. A detailed analysis of the electrical characteristics of these junctions has been recently reported.<sup>15</sup>

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**Supporting Information Available:** Experimental details, diffuse reflectance IR spectra for porous silicon derivatized with hexylMgBr/HCl and hexylLi/HCl, transmission IR spectrum for neat 1-bromo-5-(*N*-pyrrolyl)pentane, XPS spectra for hydrogen-terminated Si(100) before and after modification with 5-(*N*-pyrrolyl)pentylLi, and cyclic voltammetry of the junctions of polypyrrole with p- and n-type silicon (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>. JA990260K

(12) Freeman, P. K.; Hutchinson, L. L. *J. Org. Chem.* **1980**, *45*, 1924–1930.

(13) The electrochemical polymerization was performed using Pt mesh as a counter electrode and a solution of 0.1 M LiClO<sub>4</sub> and 0.05 M pyrrole in CH<sub>3</sub>CN at a current density of 0.5 mA/cm<sup>2</sup> ( $\sim 600$  mV vs Ag/AgNO<sub>3</sub>) for 400 s. The surface area of the electrode was 0.2 cm<sup>2</sup>, and the resulting polymers were  $\sim 2.5$   $\mu\text{m}$  thick based on coulometry. The rms roughnesses in Figure 2c and 2d were 25 and 219 nm, respectively.

(14) A similar result was reported for polypyrrole films on gold. Polypyrrole deposited on gold modified with an *n*-alkanethiol exhibited similar characteristics to that formed on bare gold. See refs 7a and 7b.

(15) Vermeir, I. E.; Kim, N. Y.; Laibinis, P. E. *Appl. Phys. Lett.*, **1999**, *74*, 3860–3862.