

Molecularly Tunable “Organic Capacitors” at Silicon/Aqueous Electrolyte Interfaces<sup>1</sup>Hua-Zhong Yu,<sup>†</sup> Sylvie Morin,<sup>‡</sup> and Danial D. M. Wayner\*

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Robust and uniform *n*-alkyl monolayers were formed on silicon from the reaction of Grignard reagents (*n*-C<sub>*n*</sub>H<sub>2*n*+1</sub>MgBr, *n* = 2, 6, 10, and 15) with hydrogen-terminated Si(111). The capacitive properties of these organic thin films on silicon in contact with aqueous electrolytes were evaluated by electrochemical impedance measurements. In particular, the reciprocal capacitance of the organic thin film modified silicon/aqueous electrolyte interfaces is proportional to the film thickness, which is tunable by simply varying the alkyl chain length. The derived dielectric constant of these organic thin films from the best fit of the reciprocal capacitance vs ellipsometric film thickness plot is  $\epsilon = 3.3 \pm 0.6$ .

## Introduction

Organic modification of oxide-free silicon surfaces offers a direct combination of molecular materials and solid-state semiconductor structures, making it an attractive approach to provide technologically useful and molecularly tunable thin films.<sup>2</sup> The fabrication and characterization of these organic thin films covalently bound to silicon surfaces promise to improve the stability toward oxidation and to maintain satisfactory electrical properties of silicon electrodes,<sup>3,4</sup> to achieve ideal surface passivation,<sup>5</sup> as well as to optimize the performance of diodelike silicon/conducting polymer junctions.<sup>6,7</sup> Particularly in the field of biotechnology,<sup>8</sup> crystalline silicon is an attractive alternative substrate for the biological microchip fabrication because of its ultrahigh purity, its well-defined structure, and the opportunity to take the full advantage of existing micro-electronic technology. The construction and characterization of robust, molecularly controllable surfaces for attachment strategies of biological macromolecules are of primary importance for the future development of silicon-based chemical or biological sensor devices. Recently, great progress has been made in the exploration of new synthetic routes to covalently attach organic molecules to silicon surfaces via S–C bonds.<sup>4,9–13</sup> In contrast, limited experimental characterization of the electrochemical properties of organic-modified silicon surfaces is available.<sup>3,4,6,14</sup>

In a recent publication,<sup>12</sup> we reported a new approach to form alkyl monolayers on Si(111) surfaces by direct reaction of Grignard reagents (*n*-alkylmagnesium bromides) with hydrogen-terminated silicon, Si(111)H. The excellent chemical stability and surface homogeneity of these organic thin films were confirmed with Si(111)C<sub>10</sub>H<sub>21</sub> as an example. Following the

same strategy, a series of monolayers on silicon with different alkyl chain lengths (*n*-C<sub>*n*</sub>H<sub>2*n*+1</sub>MgBr, *n* = 2, 6, 10, and 15) was fabricated using the same approach. Herein we report our first study of the electrical properties of these organic thin films at silicon/electrolyte interfaces. By combined experimental studies of surface properties, film thickness, and electrochemical capacitive behavior, we are able to correlate the differential capacitance of these organic thin films with their molecular structure, i.e., the number of carbons in the alkyl chain.

## Experimental Section

Silicon(111) wafers (0.99–1.25 Ω·cm, n-type, Virginia Semiconductor Inc.) were cleaned in 3:1 concentrated H<sub>2</sub>SO<sub>4</sub>/30% H<sub>2</sub>O<sub>2</sub> at 90 °C for 30 min, followed by copious rinsing with Milli-Q water. The surfaces were etched with ppb grade 40% aqueous deoxygenated NH<sub>4</sub>F (15 min) to obtain atomically flat Si(111)H.<sup>15</sup> The Si(111)H samples were then transferred, without rinsing, into the reaction vessels containing 5 mL of deoxygenated *n*-C<sub>*n*</sub>H<sub>2*n*+1</sub>MgBr (0.5–2.0 M solutions in diethyl ether, and *n* = 2, 6, 10, and 15, respectively). The reaction tubes were warmed for 16 h at 85 °C. The modified silicon samples were then rinsed with 1% CF<sub>3</sub>COOH/THF, Milli-Q water, and trichloroethane before characterization. Surfaces prepared in this way have been shown to be both oxide and metal free.<sup>12</sup>

Surface wettability measurements were performed with a contact angle goniometer (model: Cam-Micro, Tantec Inc., IL) under ambient conditions (18–22 °C, 50–60% relative humidity) using a columniated horizontal light beam to illuminate the liquid droplet. Ellipsometric measurements were made with a VASE spectroscopic ellipsometer (J.A. Woollam Co., Inc.) over a spectral range from 400 to 700 nm. A bilayer model (the bulk silicon and the organic film) was used to evaluate the thickness from the ellipsometric data assuming that the dielectric properties of the organic films are the same as those of polyethylene.

The differential capacitance–potential (*C*–*E*) measurements were performed with an Autolab Electrochemical Analyzer

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**TABLE 1: Surface and Structural Characterization of *n*-Alkyl Monolayers on Silicon Prepared from Reactions of Grignard Reagents ( $n\text{-C}_n\text{H}_{2n+1}\text{MgBr}$ ,  $n = 2, 6, 10$ , and 15) with Hydrogen-Terminated Si(111)**

|                                    | contact angle/deg <sup>a</sup> |   | thickness/Å |                    |
|------------------------------------|--------------------------------|---|-------------|--------------------|
|                                    | H <sub>2</sub> O               | <i>n</i> -C <sub>16</sub> H <sub>34</sub> | exptl       | calcd <sup>b</sup> |
| Si-C <sub>2</sub> H <sub>5</sub>   | 90.6 ± 3.0                     | 9.00 ± 3.5                                | 4.2 ± 1.8   | 2.9                |
| Si-C <sub>6</sub> H <sub>13</sub>  | 94.2 ± 6.0                     | 14.3 ± 4.5                                | 8.8 ± 1.6   | 7.2                |
| Si-C <sub>10</sub> H <sub>21</sub> | 101 ± 7.5                      | 33.9 ± 4.5                                | 11.4 ± 1.2  | 11.4               |
| Si-C <sub>15</sub> H <sub>31</sub> | 101 ± 7.5                      | 30.7 ± 4.0                                | 16.7 ± 1.0  | 16.8               |

<sup>a</sup> The contact angles provided here are thermodynamic equilibrated contact angles, which are believed to be smaller than advancing contact angles. <sup>b</sup> The predicted monolayer thickness was calculated on the basis of the equation  $d = 1.86 + 1.30(n - 1) \cos \theta$ , where  $d$  is the thickness,  $n$  is the number of carbons in the alkyl chain, and  $\theta$  is the angle between the molecule axis and the surface normal. A tilt angle,  $\theta = 35^\circ$ , was used to calculate the thickness of the alkyl monolayer on silicon.

(model: PGSTAT30, Eco Chemie BV, The Netherlands) in a self-designed three-electrode Teflon cell. The working electrode, Si(111)H or Si(111)C<sub>*n*</sub>H<sub>2*n*+1</sub> sample was pressed against an opening in the cell bottom using an O-ring seal. The reference electrode was a Pd wire charged in 0.1 M H<sub>2</sub>SO<sub>4</sub> at -2.0 V for 3 h ( $\sim -0.30$  V vs SCE), and the counter electrode was a Pt wire. All potentials quoted below were converted to refer to an aqueous SCE.

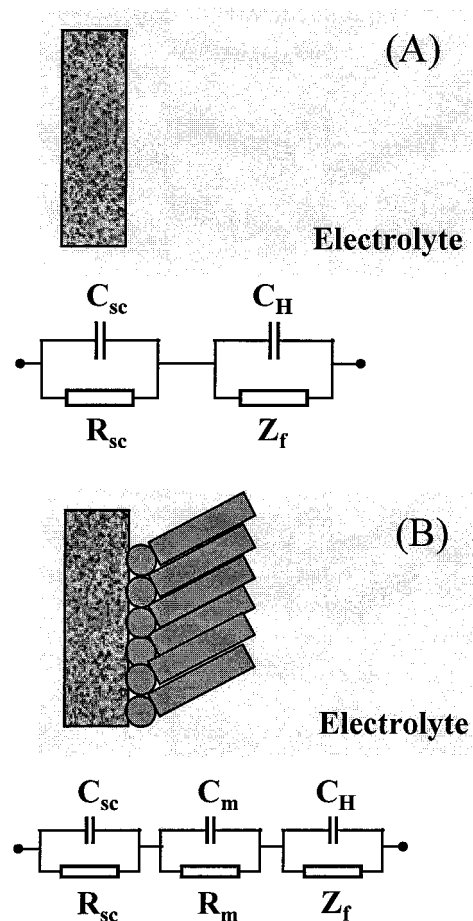
## Results and Discussion

The wetting properties of these organic thin films on silicon surfaces were examined with contact angle measurements. The silicon surfaces modified with alkyl monolayers are more hydrophobic as shown by larger contact angles obtained with H<sub>2</sub>O (Table 1) compared to that of hydrogen-terminated silicon ( $82 \pm 5^\circ$ ). With increased alkyl chain length, the hydrophobicity of the surface increases monotonically and reaches a constant value with either H<sub>2</sub>O or nonpolar organic solvent (*n*-C<sub>16</sub>H<sub>34</sub>). Together with the reproducibility of these data across the surfaces, it is reasonable to conclude that the silicon surfaces are covered with hydrophobic hydrocarbon chains uniformly over the whole wafer. The surface homogeneity is also confirmed by atomic force microscopy (AFM) images.<sup>16</sup>

Spectroscopic ellipsometry was applied as a convenient and precise means of determining the average thickness of the organic thin film on silicon in air. The data in Table 1 are averaged over at least three different samples. The measured thicknesses show a clear dependence on the alkyl chain length in the monolayer. On the basis of the Si-C and C-C bond lengths, assuming a tilt angle between the molecule axis and the surface normal, the thickness of an alkyl monolayer on silicon can be predicted. As shown in Table 1, with an average tilt angle of  $35^\circ$ , the calculated data are in good agreement with the experimental values. The larger error for the short chains may be a result of inhomogeneous coverage across the wafer due to partial oxidation<sup>17</sup> or of a greater degree of disorder and/or a greater tilt angle of chains. While it is not reasonable to expect that the tilt angle is independent of chain length, for the shortest chains, the error in the determination of the tilt angle is too large for those individual determinations to be meaningful. Nevertheless, the information regarding the structure of these monolayers is crucial to further investigate the correlation between the molecular structure and the electrical properties.

Electrochemical capacitance measurements provide an important and straightforward approach to examine the structure, as well as an opportunity to give insight into the dielectric properties of organic thin films.<sup>18</sup> The study of electrical

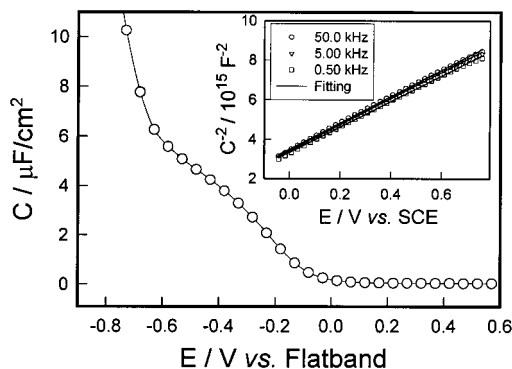
## SCHEME 1



properties of organic thin films at silicon electrode/electrolyte interfaces is a convenient alternative to solid-state measurements since it avoids preparing metal contacts on these ultrathin organic films, which is problematic. It is also essential to examine the performance of these thin films at well-defined electrochemical interfaces before more elaborate solid-state characterization should be carried out.

The electrochemical characterization of unmodified silicon, i.e., Si(111)H, provides the background for the study of electrical properties of organic thin films at silicon/electrolyte interfaces. It is well-known that the interface between a semiconductor and an electrolyte behaves like a capacitor.<sup>18,19</sup> The differential capacity of an underivatized semiconductor-concentrated electrolyte interface can be simply represented by a series of two capacitors with a resistor ( $R_{SC}$ ) and faradaic impedance ( $Z_f$ ) in parallel to account for the current flow under accumulation (Scheme 1a). Under appropriate conditions of frequency and potential, the impedance of the interface is, however, mainly capacitive, and one measures the series combination of  $C_{SC}$ , the space charge layer of the semiconductor, and  $C_H$ , the Helmholtz double-layer capacitance. Since the overall capacitance,  $C_{tot}$ , is determined by the smallest capacitor (i.e.,  $C_{tot}^{-1} = C_{SC}^{-1} + C_H^{-1}$ ), it is clear that in depletion the total capacitance is determined by the space charge capacitance ( $C_{SC}$ ) of the *n*-type semiconductor since  $C_{SC}$  will be smaller than  $C_H$ . In this case, the Mott-Schottky relationship can be applied (eq 1)<sup>20</sup>

$$C_{SC}^{-2} = \frac{2}{q\epsilon_0 N_d A_s^2} \left( E - E_{fb} - \frac{kT}{q} \right) \quad (1)$$



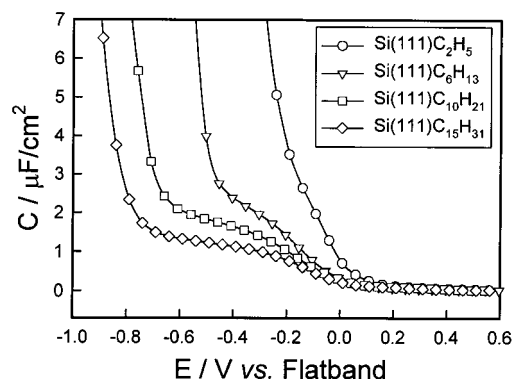
**Figure 1.** Differential capacitance of hydrogen-terminated Si(111) in contact with 0.1 M H<sub>2</sub>SO<sub>4</sub> + 2% HF as a function of electrode potential (normalized to the flat-band potential). Inset shows the Mott–Schottky plots obtained with three different frequencies (see text for details).

where  $\epsilon$  is the relative permittivity (dielectric constant) of silicon,  $\epsilon_0$  is the permittivity of free space,  $N_d$  is the dopant density of the semiconductor,  $A_s$  is the area of the electrode,  $k$  is the Boltzmann constant,  $T$  is the substrate temperature, and  $q$  is the electronic charge. In the cathodic range, where an accumulation layer is formed on the n-type semiconductor, the space charge capacitance exponentially increases as the electrode potential shifts in a negative direction (eq 2):<sup>21</sup>

$$C_{SC} = \left( \frac{q^2 \epsilon \epsilon_0 N_d}{2kT} \right)^{1/2} \exp \left( \frac{-q(E - E_{fb})}{2kT} \right) \quad (2)$$

Therefore, in the case where  $E$  is negative to  $E_{fb}$ ,  $C_H$  will dominate the overall capacitance.<sup>18</sup>

Figure 1 shows the results of differential capacitance–potential measurements of freshly prepared Si(111)H in contact with 0.1 M H<sub>2</sub>SO<sub>4</sub> + 2% HF. The insert is a Mott–Schottky plot ( $C^{-2}$  vs  $E$ ) of the above system, which enabled the determination of the flat-band potential and the dopant density. The Mott–Schottky plot exhibits no frequency dependence between 500 Hz and 50 kHz and is linear over a large potential range (−0.1 to +1.7 V vs SCE). The flat-band potential for this system,  $E_{fb} = -0.50 \pm 0.05$  V vs SCE, was obtained by extrapolating the data to infinite capacitance ( $C^{-2} = 0$ ). The dopant density,  $N_d = (4.1 \pm 0.7) \times 10^{15} \text{ cm}^{-3}$ , was calculated from the slope of the best fit. The  $N_d$  value is consistent with the dopant density derived from the four-probe resistivity measurements of the same sample. The differential capacitance–potential curve, measured at a frequency of 1.0 kHz,<sup>21</sup> and normalized to the flat-band potential is typical of that expected on the basis of the theoretical model above. When  $E > E_{fb}$ , the total capacitance is limited initially by the space charge capacitance and increases as the electrode potential approaches  $E_{fb}$ . For  $E < E_{fb}$  the capacitance tends to saturate at a value that represents the Helmholtz double-layer capacitance ( $C_H$ ). Experimentally, the saturation plateau was distorted because, in that case, the resistors in Scheme 1 decrease at negative potentials. As the potential increases beyond the onset of hydrogen evolution, current flows in the second branch of the circuit (i.e.,  $Z_f$  decreases). A hydrogen evolution current is indeed measured. This explains why the differential capacitance–potential curve is not ideally saturating to the value  $C_H$  and even strongly deviates from ideality. The steep increase of  $C$  for  $E < -0.7$  V does, in fact, correspond to the onset of fast H<sub>2</sub> evolution.<sup>18</sup> The Helmholtz double-layer capacitance at the Si(111)H surface,  $C_H = 3.7 \pm 0.5 \mu\text{F}/\text{cm}^{-2}$ , was estimated from the pseudoplateau in Figure 1.<sup>23</sup> This value is in agreement



**Figure 2.** Differential capacitance of organic thin film covered Si(111) in contact with 0.1 M H<sub>2</sub>SO<sub>4</sub> + 2% HF as a function of electrode potential (normalized to the flat-band potential).

within the experimental uncertainty with that of  $3.5 \mu\text{F}/\text{cm}^2$  reported in the literature.<sup>18</sup> We would like to remark that the discernible increase in the capacitance at a potential only slightly negative of  $E_{fb}$  indicates a very low density of electronic states at the silicon–electrolyte interface,<sup>18</sup> which is also observed in studies of the Si(111) surfaces hydrogen terminated in unbuffered HF solutions.<sup>22</sup>

Differential capacitance–electrode potential curves of silicon electrodes functionalized with alkyl monolayers (Si(111)-C<sub>n</sub>H<sub>2n+1</sub>,  $n = 2, 6, 10$ , and  $15$ ) show a very clear trend as displayed in Figure 2. The total differential capacitance was depressed gradually as the alkyl chain became longer, while the potential for onset of hydrogen evolution became more negative as seen by the negative shift of the steep increase of  $C$ . It should also be noted that these  $C$ – $V$  curves resemble that of Si(111)H and the same remarks apply. In addition, we note that the increase of the capacitance occurs immediately at the potential negative of  $E_{fb}$ . From this we conclude that the surface modification retains the low density of states at the interface.<sup>18</sup>

To evaluate the capacitive properties at these interfaces, the model that was successfully applied to the unmodified Si/electrolyte interfaces must be modified to include the alkyl film. Since these organic thin films are uniform in terms of surface properties and film thickness, it is reasonable to consider the alkyl monolayer as an organic capacitor between the semiconductor and the electrolyte (Scheme 1b). A resistor  $R_m$  must, however, be introduced in parallel to account for the presence of defects in the layer. Under appropriate conditions defined above (i.e., for  $E >$  onset for fast H<sub>2</sub> evolution), the total capacitance is represented by eq 3<sup>18</sup>

$$C_{\text{tot}}^{-1} = C_{SC}^{-1} + C_m^{-1} + C_H^{-1} \quad (3)$$

where  $C_{\text{tot}}$  is the total capacitance,  $C_{SC}$  and  $C_H$  are those determined as for the H–Si surface, and  $C_m$  is the capacitance of the organic thin film. Table 2 lists the values of the total capacitance at alkyl monolayer modified silicon/electrolyte interfaces, which were derived from Figure 2.<sup>23</sup> If it is assumed that the Helmholtz double-layer capacitance ( $C_H$ ) determined for Si–H/electrolyte interfaces is independent of the alkyl monolayer, the capacitance of the alkyl monolayers ( $C_m$ ) can be evaluated using eq 3. These values are listed in Table 2.

The capacitive behavior of an alkyl monolayer on silicon has been described above as that of an ideal organic capacitor for which the reciprocal capacitance of unit area is given by

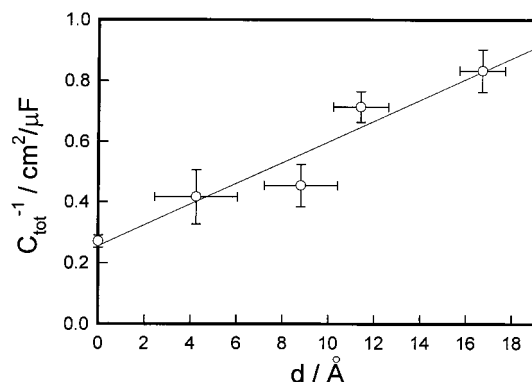
$$C_m^{-1} = d/(\epsilon \epsilon_0) \quad (4)$$



**TABLE 2: Differential Capacitance–Potential Properties of *n*-Alkyl Monolayers on Silicon (Si–C<sub>*n*</sub>H<sub>2*n*+1</sub>, *n* = 2, 6, 10, and 15) in Contact with 0.1 M H<sub>2</sub>SO<sub>4</sub> + 2% HF Electrolytes**

|                                    | differential capacitance             |                                    | Mott–Schottky measurements <sup>a</sup>           |                          |
|------------------------------------|--------------------------------------|------------------------------------|---|--------------------------|
|                                    | C <sub>tot</sub> /μF/cm <sup>2</sup> | C <sub>n</sub> /μF/cm <sup>2</sup> | N <sub>d</sub> /10 <sup>15</sup> cm <sup>−3</sup> | −E <sub>fb</sub> /V(SCE) |
| Si–C <sub>2</sub> H <sub>5</sub>   | 2.4 ± 0.5                            | 6.8 ± 1.5                          | 4.0 ± 0.2   | 0.92 ± 0.05              |
| Si–C <sub>6</sub> H <sub>13</sub>  | 2.2 ± 0.3                            | 5.4 ± 1.2                          | 4.1 ± 0.5   | 0.68 ± 0.20              |
| Si–C <sub>10</sub> H <sub>21</sub> | 1.4 ± 0.2                            | 2.3 ± 0.5                          | 3.9 ± 0.2   | 0.48 ± 0.05              |
| Si–C <sub>15</sub> H <sub>31</sub> | 1.2 ± 0.2                            | 1.8 ± 0.4                          | 3.8 ± 0.2   | 0.47 ± 0.05              |

<sup>a</sup> The dopant density  $N_d$  and the flat-band potential  $E_{fb}$  (vs SCE) were calculated from the fitting of Mott–Schottky plots ( $C^{-2}$  vs  $E$ ; see text for details). The dopant density calculated from four-point probe resistivity data on these samples was  $N_d = (3.7 \pm 0.6) \times 10^{15} \text{ cm}^{-3}$ .

**Figure 3.** Reciprocal total capacitance at *n*-alkyl monolayers modified Si(111)/0.1 M H<sub>2</sub>SO<sub>4</sub> + 2% HF interfaces as a function of the film thickness. The solid line is a least-squares fit to the experimental data (see text for details).

where  $d$  and  $\epsilon$  correspond to the thickness and the dielectric constant of the *n*-alkyl monolayer, respectively, and  $\epsilon_0$  is the permittivity of free space.<sup>24</sup> Thus, according to eqs 3 and 4, a plot of  $C_{tot}^{-1}$  versus  $d$  should be linear with a slope of  $1/(\epsilon\epsilon_0)$  and an intercept of  $1/C_H$  ( $C_{SC}$  is large and can be ignored; see above). As shown in Figure 3, the plot of  $C_{tot}^{-1}$  versus the measured ellipsometric thickness is apparently linear. A least-squares fit to the data in Figure 3 gives a dielectric constant,  $\epsilon = 3.3 \pm 0.6$ . The intercept of the fit ( $0.255 \pm 0.056 \text{ cm}^2/\mu\text{F}$ ) corresponds to a capacitance value of  $3.9 \pm 0.8 \mu\text{F}/\text{cm}^2$ , which agrees with measurements on hydrogen-terminated surfaces ( $C_H = 3.7 \pm 0.5 \mu\text{F}/\text{cm}^2$ ) within the experimental error.

The experimentally evaluated dielectric constant of alkyl monolayers on Si(111) is larger than the accepted value for polyethylene ( $\epsilon = 2.3$ )<sup>24</sup> but compares reasonably well with the value of 2.6 determined in previous electrochemical studies of *n*-alkylthiolate films on Au/Cr/silicon substrates<sup>25</sup> as well as the value of 2.9 derived from the studies of *n*-alkanoic acid monolayers between two Al plates.<sup>26</sup> It is, however, smaller than the value of  $\epsilon = 7$  obtained for *n*-alkylthiolate monolayers on Au/mica substrates.<sup>27</sup> The  $\epsilon$  value of 3.3 suggests that there are vacancies in the film through which solvent/electrolyte may penetrate. Describing the molecular layer as an *effective medium*<sup>18</sup> consisting of a mixture of *n*-alkyl chains together with solvent molecules allows the determination of the volume fraction occupied by molecules ( $F_{mol}$ ). This approach assumes a uniform distribution of the molecules over the surface, with vacancies, rather than a surface covered by compact and blocking islands separated by free surface. Within this formalism, one finds  $F_{mol} = 0.85$ , while  $F_{mol} = 1$  corresponds to maximum packing (i.e., a  $2 \times 1$  layer structure). This value explains why the layer is not entirely blocking as it should and further justifies inclusion of the resistor  $R_m$  in Scheme 1b. This average value of the filling

of the layer is consistent with preliminary STM images of the Si(111)–alkyl surfaces<sup>28</sup> and has implications regarding the ability of the films to block interfacial electron transfer. Such experiments are currently underway and will help to further our understanding of these films. Nevertheless, independent of the actual dielectric constant, the present results clearly demonstrate the direct correlation between the thickness and the capacitive properties of these organic thin films and are complementary with the interfacial capacitive investigations of alkanethiol monolayers on gold.<sup>25,27,29</sup>

A few aspects of this approach deserve further discussion. As shown in Table 2, the dopant densities derived from the Mott–Schottky measurements of Si(111)C<sub>*n*</sub>H<sub>2*n*+1</sub> ( $n = 2, 6, 10$ , and 15) are the same as that of Si(111)H and are also in good agreement with the resistivity measurement. This result is consistent with the nonpolar character of a uniform covalent silicon–alkyl film.<sup>3</sup> More interesting, for the flat-band potential, there is no significant shift observed from that of Si(111)H for the longer chains ( $n = 10$  and 15). Again, this indicates that there is no surface dipole at the silicon–alkyl interface, as expected from the weak polarization of the Si–C bond,<sup>18</sup> and further confirms the low density of electronic states at the surface as noticed from Figure 2. However, for the shorter chains, particularly Si(111)C<sub>2</sub>H<sub>5</sub>, the flat-band potential is more negative compared to other monolayer assemblies. This deviation may be related to the presence of surface states at the silicon–alkyl interface.<sup>30</sup> This is currently under further investigation in our laboratory.

## Conclusions

In summary, the organic thin films formed by the reaction of Grignard reagents with Si(111)H exhibit ideal capacitive behavior at silicon electrode/aqueous electrolyte interfaces. Modulation of the length of the adsorbate molecules allows the capacitance of these organic thin films to be tuned. It is expected that it also should be possible to modulate the dielectric properties as well as the surface chemical characteristics of these organic thin films by varying the nature of adsorbate molecules (e.g., the structure of the chain or the terminal functional groups).<sup>13</sup> Although it may be too early to suggest practical applications of organic thin films on semiconductor surfaces, the present findings show the feasibility of introducing molecular tunability into silicon-based sensors and microelectronic devices.

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