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# Dielectric properties of organic monolayers directly bonded on silicon probed by current sensing atomic force microscope

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The dielectric properties of alkyl monolayers with various chain lengths [ $\text{CH}_3(\text{CH}_2)_{n-1}$  ( $n = 12, 14, 16, \text{ and } 18$ )] covalently bonded to a hydrogen terminated  $n$ -type silicon (111) surface in a nanoscale region were evaluated using current sensing atomic force microscopy (AFM). A reliable electrical contact between the alkyl monolayers and the metal-coated AFM tip was achieved under slight stress. At a force less than 2 nN, current sharply increased as the bias was scanned over a critical value, showing that breakdown took place. The breakdown voltage linearly depended on the chain length of the alkyl monolayers and the dielectric strength of 2.0 GV/m was derived from the slope of this relation. © 2003 American Institute of Physics. [DOI: 10.1063/1.1609237]

An organic monolayer on a solid substrate<sup>1</sup> offers the direct combination of molecular and rigid materials, which should be a key component in future nanotechnology such as lithography,<sup>2</sup> chemical and biological nanosensors,<sup>3</sup> and molecular electronics.<sup>4</sup> Organic monolayers fabricated on metal substrate such as self-assembled monolayers (SAM) on gold have been studied in detail and well characterized.<sup>5</sup> The organic monolayers grafted on silicon may be more important in practical applications as advanced silicon technology can be utilized. Alkyl monolayers may be able to replace the silicon oxide layer on silicon as an insulating layer. Furthermore, the alkyl chain can be easily functionalized through organic synthesis to exploit novel devices.

There are two major methods to form alkyl monolayers on silicon. One is via the Si–O–Si bond on a preoxidized Si surface using the silane-coupling reaction. The other is via the Si–C bond on a hydrogen terminated Si (111) surface using a thermal, photochemical, or electrochemical reaction.<sup>6–18</sup> The latter method is more attractive because of the following reasons: (1) the Si–C bond is expected to be more resistive for hydrolysis than the Si–O–Si bond, (2) a higher structural order is expected for the monolayer prepared by the latter method as an organic molecule directly bonds to the Si atom on the surface of a single crystal, and (3) the thickness control of the oxide is difficult in the former method. A simple fabrication route just by heating was employed in our group, and the well-ordered monolayer structure was confirmed by ATR–IR and SFG spectroscopy.<sup>19</sup>

To apply the alkyl monolayers on silicon in nanoelectronics, it is essential to understand the electric properties of the monolayers in the nanosized region. This can be achieved by using the current sensing atomic force microscope (CSAFM). The CSAFM has features of both atomic force microscopy (AFM) and scanning tunneling microscopy and

is, therefore, able to perform the electric characterization within a nanosized region.<sup>20</sup>

The dielectric strength is one of the most important properties in the field of electronic device because the reliability and performance of electronic devices are strongly dependent on this property. In the devices composed by low dielectric strength materials, electric breakdown may easily take place, leading to the irreversible damage of the device. The dielectric strength depends not only on the insulating, i.e., dielectric, material itself, but also on the substrate and the interfacial structure. The breakdown behaviors of the alkyl monolayers on metal with nm dimension have been studied. Frisbie *et al.* employed the CSAFM to study the breakdown behavior of alkyl monolayers on gold. The alkyl monolayers were found to be able to sustain fields up to 2 GV/m before breakdown.<sup>21</sup> Whitesides *et al.* fabricated a junction consisting of an alkyl monolayer supported on a silver film in contact with a second alkyl monolayer supported on a surface of a mercury drop. In this alkyl bilayer system, the breakdown occurred at about 0.5 GV/m.<sup>22</sup> The discrepancy in the dielectric strength of the alkyl molecular layers in these two reports shows the importance of the structural order of the molecular layer and the interfacial structure.

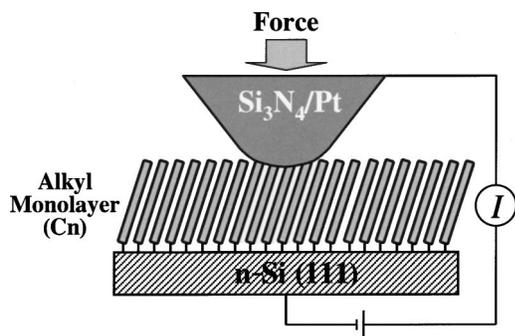
Only very little information on the electrical properties including the dielectric strength of the organic monolayers on silicon is available despite the importance of the organic monolayers grafted on silicon for practical applications as mentioned earlier.

In this letter, we measured the dielectric property of the alkyl monolayer formed on a hydrogen-terminated Si (111) via a direct covalent Si–C bond in the nanoscale region using a CSAFM with a Pt-coated tip that serves as the metal counter electrode as schematically shown in scheme 1.

Alkyl monolayers of various chain lengths were fabricated on an  $n$ -type Si (111) substrate ( $P$  doped, carrier density:  $10^{19} \text{ cm}^{-3}$ , resistivity: 0.002–0.005  $\Omega \text{ cm}$ , Shin-Etsu Semiconductor) following the procedure described in our previous letter.<sup>19</sup> The Si surface with alkyl monolayer of various chain lengths will be denoted as C12, C14, C16, and

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$$C_n = -(CH_2)_{n-1}CH_3, n = 12, 14, 16 \text{ and } 18$$

Schematic view of electric property measurement of the alkyl monolayer formed on a hydrogen-terminated Si (111) via a direct covalent Si-C bond in the nanoscale region using a CSAFM with a Pt-coated tip.

C18 for  $CH_3(CH_2)_{n-1}-Si$ ,  $n = 12, 14, 16,$  and  $18,$  respectively. The monolayer thickness was measured by ellipsometry (SOPRA GESP-5). It linearly increased with the number of methylene groups as  $1.64 \pm 0.03, 1.88 \pm 0.03, 2.06 \pm 0.05,$  and  $2.32 \pm 0.03$  nm for the C12, C14, C16, and C18 monolayers, respectively. To investigate the dielectric property of the monolayer on Si, the  $I-V$  relation was recorded using a CSAFM system (Molecular Imaging) with a Pt-coated CSAFM tip (Mikromasch,  $Si_3N_4,$  spring constant:  $0.12$  N/m). The tip was placed in contact with the monolayers with a slight stress so that a reliable electrical contact was made<sup>20</sup> and the bias was scanned. The bias is reported as a substrate potential with respect to the tip in this letter.

A typical  $I-V$  curve recorded during a bias cycle for a C16 monolayer at a force of less than 2 nN is shown in Fig. 1. When the bias was scanned negatively, a negligible current flowed until a critical bias of  $\sim 4$  V was reached. The current sharply increased at the critical bias and reached the measurement limit (10 nA). When the scan direction was reversed, the current of the measurement limit flowed until the bias was reduced to  $-2.4$  V, and then it decreased. An AFM observation after this bias scan showed the formation of an island with a few tens of nanometers in diameter and  $\sim 3$  nm in height at the position of the bias scan as presented in Fig. 2. These results suggest that the alkyl monolayer was decomposed and silicon oxide was formed by the application of the high bias.<sup>23,24</sup> This behavior can be attributed to the breakdown.

The breakdown behavior was found to be dependent on

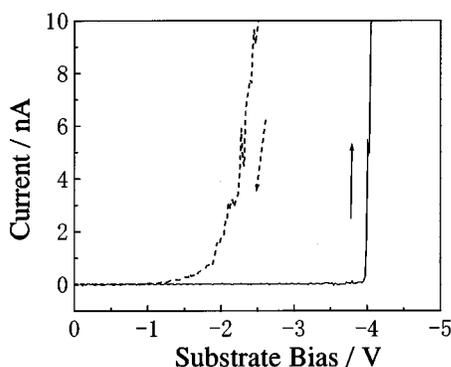


FIG. 1. A typical  $I-V$  curve of the C16 monolayer on  $n-Si$  (111) measured by CSAFM at a force less than 2 nN.

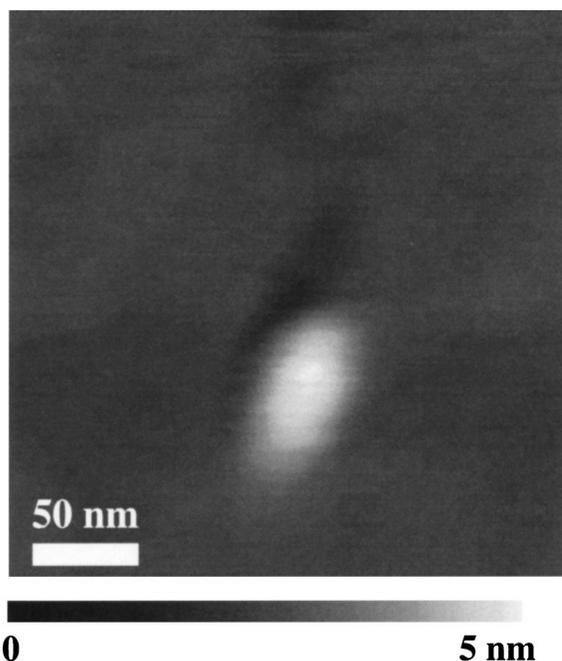


FIG. 2. An AFM image of Si (111) surface covered with the C16 monolayer recorded after the bias scan shown in Fig. 1.

the alkyl chain length, i.e., thickness, of the monolayer as shown in Fig. 3. The  $I-V$  curve shifted to more negative potential direction when the monolayer of the longer alkyl chain, i.e., the thicker monolayer, was used, resulting in the higher breakdown voltage. Figure 4 shows the thickness dependence of the breakdown voltage. The voltage is linearly related to the monolayer thickness and this linear relation can be extrapolated to the origin of the coordinates as shown in the inset of Fig. 4. This implies that the bias is mostly applied to the alkyl monolayers. The dielectric strength is the maximum potential drop within the insulator divided by the thickness of the insulator. While the potential drop occurs entirely within the alkyl monolayers in the case of the CSAFM tip/alkyl monolayer/gold junction because the alkyl monolayer is sandwiched between two metal electrodes,<sup>21</sup> it should be divided into two parts, namely, within the alkyl insulator and the semiconductor, in the present system, i.e., the CSAFM tip/alkyl monolayer/semiconductor junction. However, because of the very high doping density of the Si substrate used in this study, one can essentially neglect the potential drop within the Si substrate. Thus, the dielectric

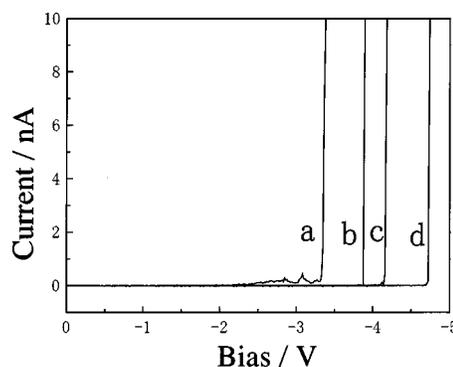


FIG. 3.  $I-V$  curves measured at the  $n-Si$  substrate covered with the (a) C12, (b) C14, (c) C16, and (d) C18 monolayers at a force less than 2 nN.

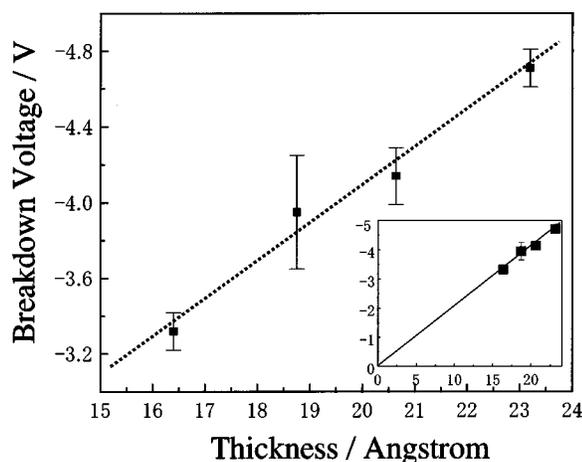


FIG. 4. Monolayer thickness dependence of the breakdown voltage.

strength of the monolayer can be obtained from the slope of the linear relation between the breakdown voltage and the monolayer thickness as 2.0 GV/m.

It is interesting to compare this value with those of silicon dioxide, which is the most commonly used dielectric material in the current silicon technology, polyethylene, which is the bulk material consisting mainly of alkyl chain, and molecular layers with alkyl chain formed on other substrates. Table I shows the dielectric strengths of the alkyl molecular layers on various substrates as well as of the silicon dioxide and polyethylene. The dielectric strength of the present system is the highest among the values of shown in Table I. It is about ten times that of the bulk polyethylene (0.16–0.23 GV/m)<sup>25</sup> and is four times that of the alkyl bilayers formed between the Hg drop and the Ag plate with physical contact ( $\sim 0.5$  GV/m)<sup>22</sup> but is the same as that of the alkylthiol SAM fabricated on gold. These results strongly suggest that the dielectric strength depends on the conformational order, i.e., the higher the order, the higher the dielectric strength. The fact that the dielectric strength of the present system is the same as that of the alkylthiol SAM on gold shows that the order of the alkyl monolayer on Si is as high as that of the alkylthiol SAM on gold, which is known to be very highly ordered.

The dielectric strength of the present system is larger

TABLE I. Dielectric strength of various systems.

Samples	Dimension (m)	Dielectric strength (GV m <sup>-1</sup> )	Ref.
Alkyl monolayer/Si	10 <sup>-8</sup>	2.0	This study
Alkyl monolayer/Au	10 <sup>-8</sup>	2.0	21
Alkyl bilayer/Ag	10 <sup>-8</sup>	0.5	22
Polyethylene	Bulk	0.16–0.23	25
SiO <sub>2</sub>	Bulk	0.8–1.3	26

than that of SiO<sub>2</sub> (0.8–1.3 GV/m),<sup>26</sup> demonstrating that the alkyl monolayer on silicon is really a very good molecular electronic material with a sufficiently high dielectric strength to be able to use an insulating layer on silicon. It is important to mention that the thickness of the insulating layer, i.e., the alkyl monolayer, on silicon can be easily tuned by controlling the number of carbon chains.

In summary, the dielectric properties of alkyl monolayers directly bonded on a hydrogen terminated silicon (111) surface in a nanoscale region were measured using the CSAFM. The breakdown voltage was found to be linearly dependent on the monolayer thickness and a dielectric strength of 2.0 GV/m for these junctions was obtained.

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