

KPAN010: Application - Hybrid Silicon-Organic Devices

“Electrochemical Characterisation of Si(111) Modified with Linear and Branched Alkyl Chains” -

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Keywords

Kelvin Probe, Work Function, WF, Surface Photovoltage, SPV, Si (111), Oxidation Resistance

Abstract

A simple chemical strategy is described to produce branched alkyl chains on Si(111) from the reaction of an ester-terminated silicon surface. The stability of the silicon surfaces with linear and branched monolayers is characterised by electrochemical impedance, Kelvin probe, and high-resolution electron energy loss spectroscopy (HREELS). The direct observation of surface states in capacitance-voltage plots can be used to monitor the growth of electrically active defects associated with oxidation of the silicon substrate. We find that the total surface state density of the freshly made surfaces increases in the following order: Si-B < Si-UDE < Si-C10 (where B is the branched structure, UDE is ethyl undecanoate, and C10 is decyl) in aqueous and organic solvent/electrolyte systems. After 24 h in the electrolyte solution, the surface state densities increase but the order remains the same. The branched structure is significantly more resistant to oxidation.



Figure 1. KP Technology KP020 with SPV010

These observations are consistent with the results of other characterisation techniques including HREELS and surface photovoltage and indicate that the branched alkyl chain-modified surfaces are considerably more stable, especially in aqueous electrolytes, making them suitable for future use in biological sensor applications.

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Research Area

The covalent attachment of organic films on oxide-free semiconductor surfaces such as silicon is of growing interest for potential applications from surface passivation to the incorporation of chemical/biochemical functionality at interfaces for use in biosensors or biosensor arrays. Much of the work reported in the literature has focused on elaborating the organic chemistry from films terminated by unreactive methyl groups to other much more reactive terminal groups such as acids or esters, amines, alcohols, and aromatic rings that can be used for further attachment of more complex organic or bioorganic structures. However, because of the mismatch between the distance between Si atoms on Si(111) (0.385 nm) and the diameter of an alkyl chain (0.42 nm), it has been obvious that the alkyl chains cannot pack 1:1 per silicon. It has been suggested that the (theoretical) maximum coverage of these monolayers is 0.5 ML (i.e., 50% substitution of the surface hydrides), although the maximum coverage of the monolayer on silicon has been the subject of some debate. Whatever the maximum number of Si-C bonds, it is clear that a significant number of unreacted Si-H sites still remain on the surface. Consequently, the surfaces are vulnerable to oxidation by water and oxygen, which can penetrate through the monolayer. This inherent instability is inconsistent with the development of stable, robust sensors, the application cited by most of the published work in this area. The problem is that oxidation of silicon can result in the formation of electrically active surface states that change the electrical properties of the underlying silicon. Any strategy that aims toward hybrid silicon-organic devices should ideally limit the number of oxide-based surface states and, at minimum, stabilize them so they do not change over time. It is reported, herein, an approach to increase the extent of alkylation of hydrogen-terminated silicon resulting in a more electrically stable Si-C interface.



Figure 2. KP Technology KP020 System with SPV010

An ester-terminated monolayer can react with alkyl Grignards, resulting in an effective doubling of the number of alkyl chains on the surface. In this paper comparisons of such a branched surface (Si-B) with two other unbranched systems, the decyl (Si-C10) and the ethyl undecanoate (Si-UDE) surfaces, on Si(111) surfaces are reported. The surfaces are characterized using electrochemical impedance and other techniques such as Kelvin probe, ellipsometry, and high-resolution electron energy loss spectroscopy (HREELS). Differential capacity measurements are performed in different electrolytes to give the comparison of dielectric properties and stability of the modified surfaces. Kelvin probe, ellipsometry and high-resolution electron energy loss spectroscopy (HREELS) provide consistent complementary results. All the results indicated that the branched alkyl chain modified surfaces are considerably more resistant to oxidation, making them suitable for future development of biological sensor applications.



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Use of Kelvin Probe

A KP Technology Kelvin probe was used to measure the Surface PhotoVoltage Measurements (SPV), which provides a direct measure of band bending (the difference in the surface potential in the dark and under illumination). A white light fibre optic source was used to illuminate the modified silicon surface, ensuring that the light was of sufficient intensity to saturate the photovoltage

SPV measurements were performed using a Kelvin probe to measure the difference in the surface potential in the dark and under illumination. On a semiconductor surface, surface charges give rise to long-range electric fields that penetrate a substantial distance into the material giving rise to band-bending. Surface states, electronic states within the bulk band gap and therefore spatially localised to the surface, can act as charge traps for electrons (or holes) giving rise to band bending. Under illumination, photogenerated electron hole pairs act to screen the surface charge responsible for any band bending, flattening the bands (provided that the light intensity is sufficient). The SPV is therefore a measure of the surface charge or density of occupied surface states. Freshly etched H-terminated Si(111) surfaces typically show a very low SPV (<30mV), as expected for surfaces with a low density of surface states.

Alkyl-terminated Si(111) is expected to maintain the minimal band-bending observed on the H/Si- (111) surfaces due to the nonpolar nature of the Si-C bond. The SPVs of freshly made Si-C10, Si-UDE, and Si-B are 80, 80, and 44 mV as shown in Table 1. The uncertainty is (20 mV. For the doping density of the silicon used in the present experiments ($3.5 \times 10^{15} \text{ cm}^{-2}$), this degree of band bending corresponds to a density of trapped charge of $<5 \times 10^{10} \text{ cm}^{-2}$. Somewhat surprisingly, fewer charges appear to be trapped on Si-B surfaces than on Si-C10 and Si-UDE surfaces, although this difference is barely outside of the experimental uncertainty. As these SPVs are seen to decrease upon dipping in HF, most of these surface states are attributed to extrinsic oxidation of the interface during the modification reactions. The values in parentheses in Table 1 are the SPVs of the three different modified surfaces after 17 h in water. The photovoltage of Si-B surface remains constant (40 mV) while those of Si-C10 and Si-UDE surfaces increased significantly from 80 to 160 and 140 mV, respectively. These results indicate that water or oxygen molecules are capable of penetrating through the shorter nonbranched monolayers and oxidising the Si surface, while the Si-B surface is much more stable, and the branched alkyl monolayer provides much better blocking properties.



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Conclusion

In this paper, a detailed characterisation of decyl, ethyl undecanoate, and branched alkyl monolayer-modified silicon surfaces using electrochemical measurements is presented. Flat band potentials, dielectric properties, and surface state analysis from the differential capacitance-potential curves showed that the branched alkyl monolayer with higher alkyl density provides excellent chemical and electrical passivation to the silicon electrode surfaces. Kelvin probe and HREELS measurements provide the complementary consistent results. The much better stability of the branched alkyl chain monolayer-modified surfaces provides an alternative to the formation of organic monolayers suitable for incorporation into silicon-organic hybrid sensors.

Reference

1. Original publication: *"Electrochemical Characterization of Si(111) Modified with Linear and Branched Alkyl Chains"* -

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Testimonial

"The KP Technologies Kelvin probe is an easy to use system that has proven to be extremely powerful and useful for characterizing the electronic properties of organic semiconductor interfaces. It has quickly become an indispensable tool in our laboratory."

- Dr. Greg Lopinski

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