Theoretical Investigation of the Energetics, Structure and Coverage of Alkylated and Methoxylated Silicon (111) Surfaces

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Functionalized silicon (111) surfaces have a wide variety of applications in molecular electronics, sensing, photoelectrochemistry, chemical and electrical surface passivation, porous silicon photoluminescence and control of photopatterning. This project is a comprehensive study of the energetics, structure and coverage of silicon (111) surfaces functionalized with the alkyl groups methyl, ethyl, hexyl, octyl, iso-propyl, tert-butyl, and phenyl and with the methoxy group. In all cases, the surface geometry and the free energy of formation for the most probable mechanisms involving hydrogenation-chlorination-Grignard alkylation were calculated for surface coverages ranging from 25% to 100%.

The most interesting finding was the formation of a full stacking fault on the terraces of the methylated surface (see Figures 1 and 2). STM images of this surface taken at 4.7 K, indicated that the torsion angle of the methyl group with respect to the subsurface silicon layer is $\phi=23 \pm 3^{\circ}$. Repulsions between hydrogen atoms in adjacent methyl groups are minimum at 30º, while repulsions between hydrogen atoms and second layer silicon atoms are minimum at 60º. The experimental result of 23º was surprising because it suggests a tendency of the methyl group towards the eclipsed configuration (0º) rather than staggered (60º). In contrast, quantum mechanical Density Functional Theory calculations gave an equilibrium torsion angle of 37.5º, indicating a tendency towards the staggered configuration. This discrepancy was resolved by showing that the CH$_3$ on the step edges and etch pits interacts repulsively with the CH$_3$ on the surface, inducing the formation of a stacking fault between the 1$^{st}$ and 2$^{nd}$ silicon layers of the Si(111)-CH$_3$ surface terraces. This could occur during the chlorination-alkylation of the Si(111)-H surface. This stacking fault model predicts $\phi=22.5^{\circ}$ measured with respect to the bulk (corresponding to $\phi=37.5^{\circ}$ with respect to the second layer Si atoms). The model can be tested by measuring the orientation of the CH$_3$ within the etch pits, which will have $\phi=37.5^{\circ}$ or by making a surface without etch pits, which will have $\phi=37.5^{\circ}$.
Figure 1. Illustration of the step edge transformation that occurs on the Si(111)-CH$_3$ surface upon the formation of the stacking fault on the terraces. The emergence of the stacking fault is only favorable in the presence of step edges. Blue = hydrogen, gray = carbon, orange = silicon.

Figure 2. Top view of the CH$_3$-terminated Si(111) surface, at 25%, 50%, 75%, and 100% coverage. The sites not occupied with methyl were terminated with hydrogen atoms. The dotted lines show the 2x2 unit cell used in the calculations. As the packing density $\theta$ rose, the torsion angle shifted from $\sim 59.9^\circ$ at 25% to $\sim 37.1^\circ$ at 100%. Note that the torsion angle for the structure with 50% coverage was measured counterclockwise from the Si-Si bond, while it was measured clockwise for 25%, 75% and 100%. This is because in each case there exist two energetically equivalent structures: one in which the angle of interest (between 0$^\circ$ and 60$^\circ$) occurs in the clockwise direction and one in which it occurs in the counterclockwise direction. In a simulation, both energy minima are equally likely to occur. Blue = hydrogen, gray = carbon, orange = first layer silicon, and yellow = second layer silicon.