

Controlled Silicon Surface Functionalization by Alkene Hydrosilylation

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Supporting information

1. Experimental details:

Double-side polished n-doped silicon (111) and (100) wafers (resistivity $\sim 30 \Omega\text{.cm}$) are cut from a 500 μm thick sample with rectangular shapes for infrared spectroscopy. Each sample is cleaned according to the standard RCA procedure: immersion into 1) a solution of $\text{H}_2\text{O}:\text{H}_2\text{O}_2:\text{NH}_4\text{OH}$ (4:1:1 by volume), where H_2O is deionized water (DIW) ($\rho = 18.2 \text{ M}\Omega\text{.cm}$), and 2) a solution of $\text{H}_2\text{O}:\text{H}_2\text{O}_2:\text{HCl}$ (4:1:1). In both cases, the solutions are heated for 10 min at 80°C and the silicon (Si) samples are rinsed with profuse DIW after each steps. After these two standard cleans (SC-1 and SC-2, respectively),¹ the samples have a thin oxide ($\sim 8\text{-}10 \text{ \AA}$). Oxide-free, atomically flat H-terminated H/Si(111) are then obtained by etching with hydrofluoric acid ($\sim 20\%$) for 30s, followed by etching in ammonium fluoride (49%) for two and a half minutes. Oxidized, flat silicon (100) surface ($\text{SiO}_2/\text{Si}(100)$) is hydrogen-terminated by immersing the sample after the SC-1 and SC-2 cleans (i.e. while they are still oxidized) in a solution of triethoxysilane and anhydrous toluene (1:19) at 80°C for at least 14 hours. In order to control the moisture, the experiments are performed in a nitrogen (N_2)-purged glove box. To grow a thinner oxide layer ($\sim 6 \text{ \AA}$), H-terminated Si(100) samples (after HF etching) are immersed in $\text{H}_2\text{O}_2:\text{H}_2\text{SO}_4$ (1:4) at 80°C for 10 minutes. Hydrogenation is then performed in a similar fashion (using triethoxysilane and anhydrous toluene).

Two different ways are used to immobilize the indene ligand (1-5 mg in 20 ml solvent), shown in Fig. S1, onto the H/Si(111) and H/SiO₂/Si(100): 1) the H/Si samples

¹ Higashi, G. S., Chabal, Y. J. *Silicon Surface Chemical Composition and Morphology* in *Handbook of semiconductor wafer cleaning technology*, Kern, W., Ed.; Noyes publications: East Windsor, **1993** 433-496

are immersed in a solution of indene ligand with either IPA or chlorobenzene and 1-5 mg H₂PtCl₆ (as a catalyst) for 4 hours at 80°C; and 2) the H/Si surface, in solution with the indene ligand dissolved in chlorobenzene, is irradiated with UV-light (254 nm) 2 hours on each side in a N₂-purged environment (the sample is turned over for irradiation of the other side at half-time). The immobilization is followed by a 5 min-sonication and a thorough-rinse in chlorobenzene to remove any molecules that have not reacted with the surface. Different UV wavelengths (254 and 365 nm) and irradiation times (2, 4 and 6h) have been used (see section 3 and 4).

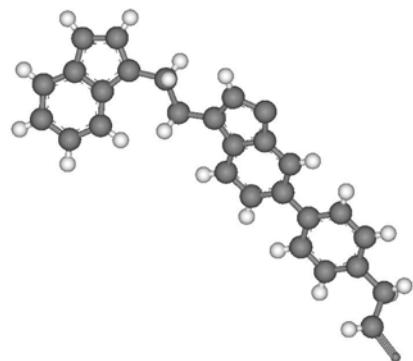


Figure S1. Indene ligand

2. Isopropanol reactivity with H-terminated surfaces:

Figure S2 shows the results of immersion of H/Si(111) (left panel) and H/SiO₂/Si(100) (right panel) in (a) isopropanol (IPA) only, (b) IPA with catalyst and (c) IPA with catalyst (H₂PtCl₆) and indene ligand for 4 hr. All the spectra are reference to the initial H-terminated Si surfaces, H/Si(111) and H/SiO₂/Si(100) respectively, so that negative features indicate a loss of species.

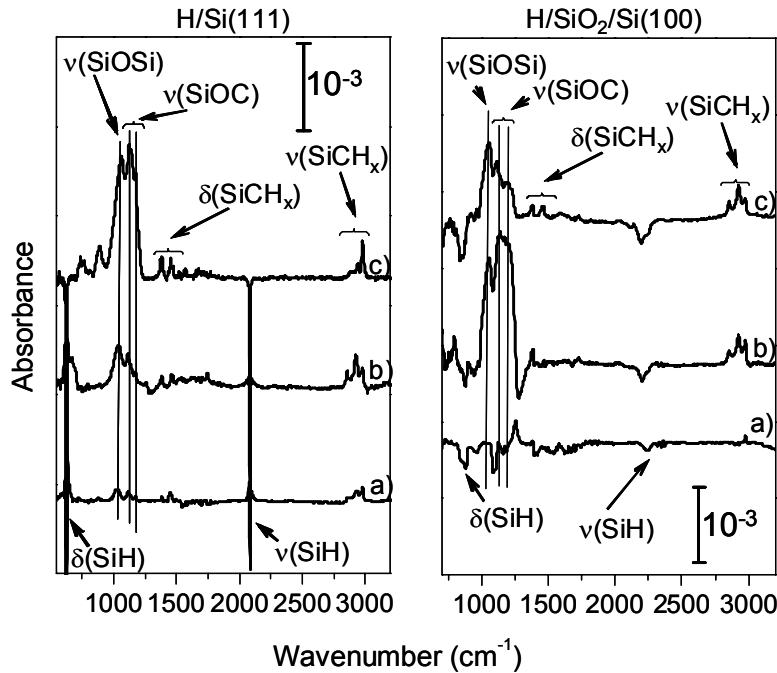


Figure S2. Transmission infrared spectra of a) isopropanol only, b) isopropanol and H₂PtCl₆, and c) isopropanol with H₂PtCl₆ and indene ligand on (left) H/Si(111) and (right) H/SiO₂/Si(100)

For H/Si(111) surface, IPA clearly reacts with the surface: there is a loss of both stretching (2083 cm⁻¹) and bending (626 cm⁻¹) Si-H vibrations, indicating reaction of surface hydrogen, and absorbance features associated to IPA bonded to the Si surface are observed, such as the Si-O-C asymmetric stretching mode at 1116 cm⁻¹, the Si-O-C rocking mode at 1174 cm⁻¹, the CH_x stretching modes in the 2800-2950 cm⁻¹ region, and CH_x deformation modes at 1382 and 1440 cm⁻¹. More IPA reacts with the surface (~60% monolayer of H is removed) when the catalyst (H₂PtCl₆) is used than for IPA (~ 25% of the hydrogen is removed). It therefore appears that the presence of H₂PtCl₆ promotes the reaction of IPA with the surface. Additionally, more Si-O-Si (silicon oxidation) is formed when the catalyst is present. When the ligand is added (Fig. c), the surface is fully reacted

with alkyl groups (complete loss of hydrogen and presence of alkyl modes), *with no evidence for ligand attachment*.

Similar results are observed for the oxidized surface, H/SiO₂/Si(100): IPA reacts without the presence of the catalyst (H₂PtCl₆), and the indene ligand does not react.

3. Time dependent studies of UV-light treatment:

Transmission infra red spectra of the indene-ligand immobilization with UV-light (254 nm) are shown in Fig. S3 for different irradiation times: (a) 1 hr, (b) 2 hr, and (c) 3 hr for each side of the H/Si(111) sample, for a total exposure of 2, 4, and 6 hours,

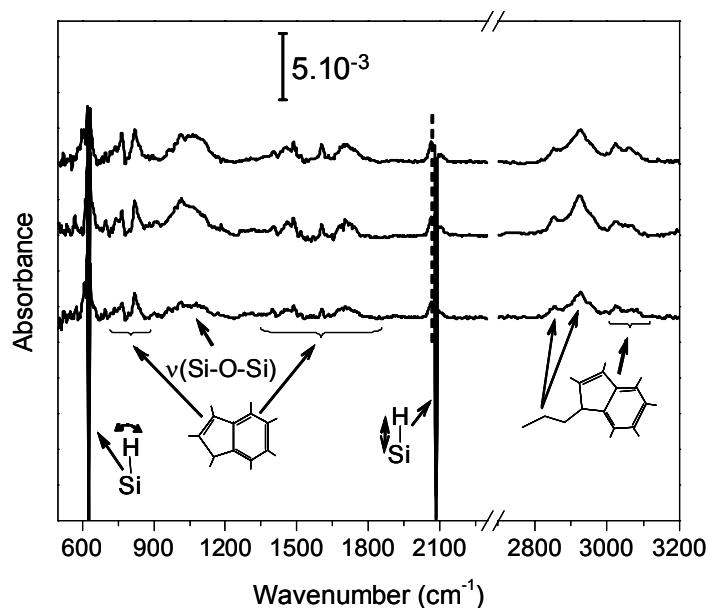


Figure S3. Transmission infrared spectra of chlorobenzene and indene ligand for different reaction times of UV irradiation: a) after 2h, b) 4h, and c) 6h on H/Si(111) surface.

respectively. The spectra presented are all referenced to the H/Si(111) surface. Surface hydrogen is removed by reaction, as evidenced by the negative features at 2083 cm⁻¹ (Si-H stretch mode) and 626 cm⁻¹ (Si-H bend mode), while absorbance features related to the indene ligand are clearly present: 750-900 cm⁻¹ and 1300-1700 cm⁻¹ are the bending mode regions, and 3000-3100 cm⁻¹ the stretching mode region of the indene group. C-H stretch modes are also observed between 2800-3000 cm⁻¹. The hydrogen is not completely removed. Instead its environment changes as evidenced by broad features centered around 2065 cm⁻¹ and 626 cm⁻¹, typical of Si-H surrounded by reacted Si atoms.

Using the total area of the Si-H and oxide modes (see section 5 below), the amount of hydrogen reacted with the ligand can be estimated: a) after 2 hr of UV exposure, about 25% of the hydrogen is lost, with 20% replaced by the indene ligand; b) after 4 hr of UV exposure, ~ 40% of hydrogen is removed and 30% of the total surface is functionalized with the organic ligand (maximum concentration observed); and c) after 6 hr of UV exposure, there is no increase in ligand coverage or H loss. The broad feature observed at 1050 cm^{-1} corresponds to Si-O-Si bonds (silicon oxide). Comparing the integrated area to that of a 10 \AA oxide, we estimate the average thickness of the total amount of silicon oxide to $\sim 0.4\text{ \AA}$ but the surface area occupied by this oxide is $\sim 10\%$.

4. **Wavelength dependence for the UV irradiation process on different surfaces:**

Figure S4 (a and b) compares the degree of indene ligand immobilization for two different UV wavelengths (365 nm and 254 nm) on the oxide-free H/Si(111) surface, and Fig. S4(c) shows the result of 254 nm UV irradiation of the hydrogen on the oxidized surface, H/SiO₂/Si(100). For S4 (a and b), the irradiation time is 4 hr. In both cases, all the indene-ligand features discussed earlier are present. However, the extent of the reaction varies: for $\lambda = 365\text{ nm}$, only 30% of the surface hydrogen is removed ($\sim 20\text{-}25\%$ ligand attached), while for $\lambda = 254\text{ nm}$ $\sim 40\%$ of hydrogen is removed with $\sim 30\%$ of the surface reacted with ligand. This indicates that the reaction rate is slower at 365 nm than at 254 nm, resulting in a lower ligand coverage for similar irradiation times. Interestingly, less oxidation occurs with 365 nm. In the absence of ligand, the H/Si(111) surface in solution in chlorobenzene remains stable under UV irradiation with less than 3% H removal after 2 hours irradiation on each side (4 hours in total).

Figure S4 (c) shows that no ligand immobilization occurs on H/SiO₂/Si(111) with 254 nm UV-light: absence of ligand features at $750\text{-}900\text{cm}^{-1}$, $1300\text{-}1700\text{cm}^{-1}$ and $3000\text{-}3100\text{ cm}^{-1}$ in spectrum S3(c). This observation, together with the data in Fig. 2(c) of the main article for the H/SiO₂/Si(100) surface, confirms that it is the presence of a thin oxide layer (and not the substrate orientation) that prevents ligand immobilization. The absence of ligand reaction under these conditions supports the electron-hole (exciton) model proposed in the main text.

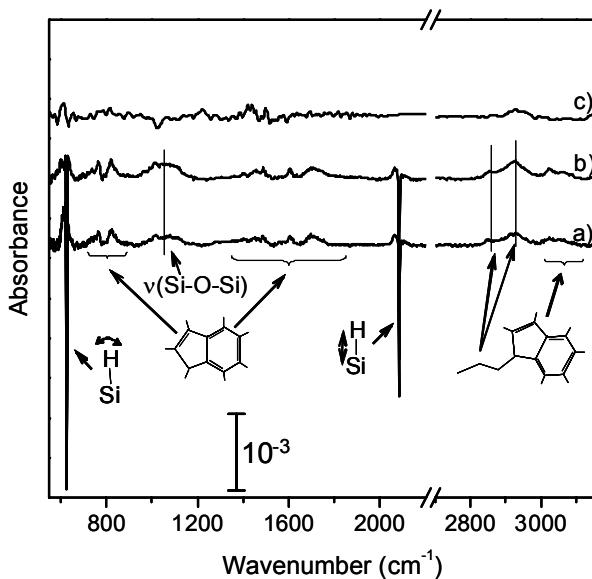


Figure S4. Transmission infrared spectra of chlorobenzene and indene ligand for different wavelengths of UV irradiation: a) 355nm, and b) 254nm on H/Si(111) surface, c) 254nm on H/SiO₂/Si(100)

5. Estimation of the indene-ligand coverage:

Estimating the ligand coverage is difficult because both ligand reaction (immobilization by hydrosilylation) and surface oxidation take place during the overall reaction cycle. The loss of hydrogen cannot therefore be strictly related to ligand reaction. To address this issue, a surface with the highest ligand coverage (i.e with ~40% hydrogen removed) was exposed to air for 15 hours to further remove hydrogen by oxidizing the surface. The increase oxide absorption (Si-O-Si modes at 1050 cm⁻¹) and the further loss of hydrogen (decrease of Si-H bending and stretching modes) were measured. The data show that 12% loss of the Si-H integrated area with an associate increase of 0.047 cm⁻¹ for the integrated area of the Si-O-Si mode. From these data, the conversion between Si-O-Si integrated area and surface coverage is estimated to be 0.39 cm⁻¹ /monolayer. Using this conversion, the area covered by oxide is found to be ~10% when 40% of the Si-H is removed, indicating that 30% of the surface has reacted with the indene ligand.

6. Stability of the indene ligand:

Since both ligand immobilization and silicon oxidation take place under most reaction conditions, the surface is not perfectly homogeneous. It is therefore important to investigate the stability of the immobilized indene ligand to chemical attack, including HF etching. The H/Si(111) surface with ~30% immobilized ligand (Fig. S5a) was subjected to very harsh basic (SC-1) and acidic (SC-2) oxidizing treatments² consisting of H₂O:H₂O₂: NH₄OH (4:1:1) and H₂O:H₂O₂:HCl (4:1:1), respectively, at 80°C for 10 minutes each, with thorough DWI rinsing prior and following each treatment. Such procedures are effective to remove hydrocarbons, metallic impurities and particles and

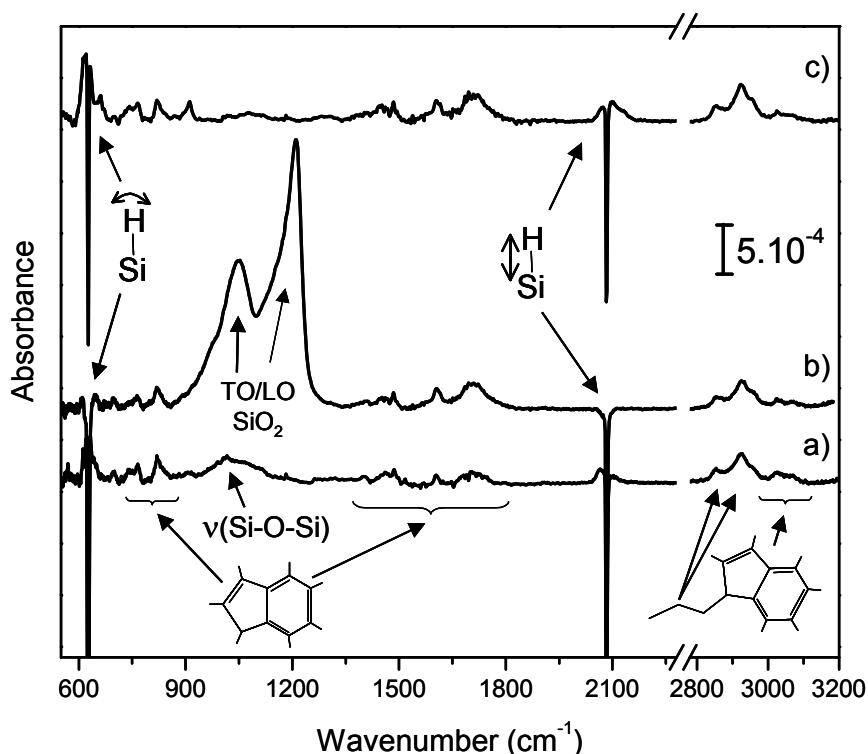


Figure S5. Transmission infrared spectra of chlorobenzene and indene ligand using UV light as a catalyst on H/Si(111) a) before any etching, b) after SC-1 and SC-2 treatments, and c) SC-1 and SC-2 treatments followed by HF etching, on H/Si(111) surface.

usually result in complete oxidation of silicon surfaces. Fig. S5(b) shows strong SiO₂ TO

² Higashi, G. S., Chabal, Y. J. *Silicon Surface Chemical Composition and Morphology* in *Handbook of semiconductor wafer cleaning technology*, Kern, W., Ed.; Noyes publications: East Windsor, **1993** 433-496

and LO phonon bands, but there is no evidence for removal of the indene ligand. When this oxidized surface is immersed in HF, the oxide is completely removed, but again the ligand remains unperturbed. These remarkable results show that the Si-C bond between the indene ligand and the substrate is resistant to the harshest chemical treatments.

7. Activity of catalyst in chlorobenzene:

Both H/Si(111) and H/SiO₂/Si(100) show evidence of indene reaction when the hydrogen-terminated Si surface is immersed in chlorobenzene with H₂PtCl₆ as a catalyst. Stretching and bending modes related to the indene ligand molecules are clearly observed (see Figure S6). On H/Si(111), the removal of hydrogen is complete and ~ 25% of ligand molecules are bonded to the surface suggesting that ~ 75% of the silicon surface form Si-O-Si bond. For H/SiO₂/Si(100), about 55% of SiH has reacted, with about ~ 20% ML of ligand attached. Since the reference is the H/SiO₂/Si(100) surface, the negative feature at 2960 cm⁻¹ is attributed to ethoxy groups from the triethoxysilane that have not reacted.

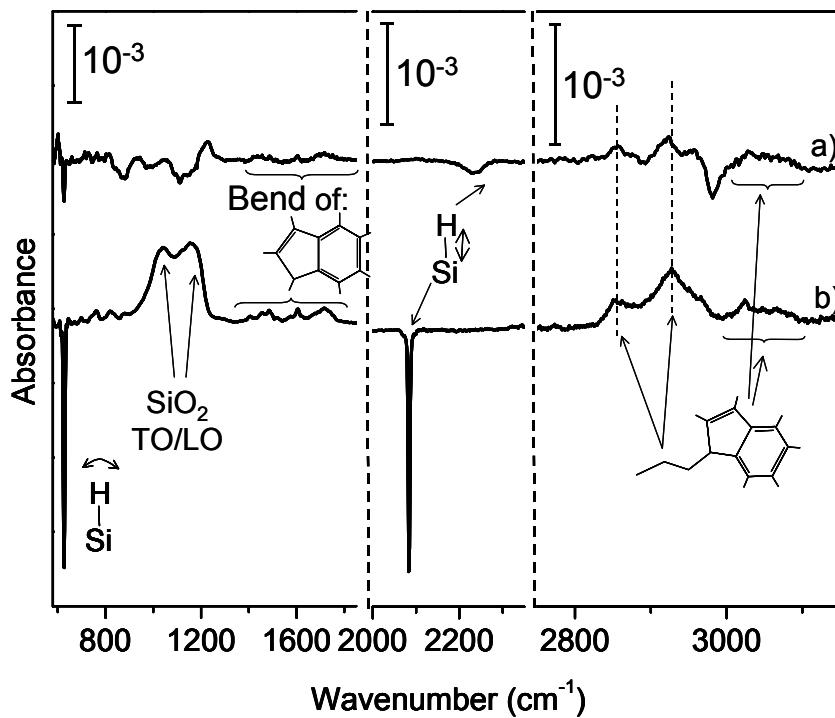


Figure S6. Transmission infra red spectra of chlorobenzene, indene ligand using H₂PtCl₆ as a catalyst on a) H/SiO₂/Si(100) and b) H/Si(111)