Determination of the bonding of alkyl monolayers to the Si(111) surface using chemical-shift, scanned-energy photoelectron diffraction

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The bonding of alkyl monolayers to Si(111) surfaces has been studied by conventional x-ray photoelectron spectroscopy (XPS) and chemical-shift, scanned-energy photoelectron diffraction (PED) using synchrotron radiation. Two very different wet-chemical methods have been used to prepare the alkyl monolayers: (i) olefin insertion into the H–Si bond on the H–Si(111) surface, and (ii) replacement of Cl on the Cl–Si(111) surface by an alkyl group from an alkyllithium reagent. In both cases, XPS has revealed a C 1*s* signal chemically shifted to lower binding energy, which we have assigned to carbon bonded to silicon. PED has shown that both preparative methods result in carbon bonded in an atop site with the expected C–Si bond length of 1.85 ± 0.05 Å. Chemical-shift, scanned-energy photoelectron diffraction is a particularly valuable probe of local structure at surfaces that contain the same element in multiple, chemically distinct environments. © *1997 American Institute of Physics*. [S0003-6951(97)04134-X]

The chemical reactivity of hydrogen-terminated Si(111) [H–Si(111)] and chlorine-terminated Si(111) [Cl–Si(111)] surfaces toward several organic reagents[1–3] may open exciting technological opportunities in the electronic sensing and control of complex molecular processes. In the work reported here, we have used chemical-shift, scanned-energy photoelectron diffraction[4,5] to determine the local bonding geometry of a C–Si bond formed between an alkyl group and a silicon substrate.

However, carbon photoelectron diffraction (PED) would be difficult to interpret because there are multiple carbon atoms in the alkyl adsorbate. For the case of multiple atoms of the same element located in different sites on a surface, Weiss *et al*.[6,7] have demonstrated the utility of reconstructing the scanned-energy PED signal of just one type of site by first decomposing the core level photoemission spectrum at each photon energy into its chemically shifted components. The observed intensity modulations of each component are then used to determine the local bonding geometry of each chemically different surface species. Our use of this technique in this letter is the first example of its application to functionalized surfaces created using standard wet chemical methods.

Two distinct synthetic methods are explored in this letter:

(i) the reaction between an olefin and H–Si(111)[1,2] illustrated with 1-pentene; and
(ii) the reaction between an alkyl–lithium reagent and Cl–Si(111)[3] illustrated with methyllithium.

In the first case, a fused silica cuvette was filled with 4 ml 1-pentene (Aldrich, 99%) and a shard of freshly prepared H–Si(111).[2] The cuvette was sparged with argon until half of the pentene had evaporated. The silicon surface was illuminated for 2 h with a mercury arc lamp (185 and 253.7 nm, Jelight 80-2049-2 pen lamp), removed, rinsed with ethanol, then water, and finally, dried.

In the case of the second synthetic method, we formed the required Cl–Si(111) by placing freshly prepared H–Si(111)[2] in a fused silica cuvette, evacuating to $<6 \times 10^{-6}$ Torr, then exposing to 0.2 Torr Cl_2 (Matheson, 99.99%) and illuminating for 15 s with a broadband 350 nm lamp (Spectronics, MB-100, fluorescent flood).[8] After removing the Cl_2 and backfilling with Ar, methyllithium (1.4 M in diethyl ether, Aldrich) was transferred by canula onto the sample. After exposures ranging from 5 min to several hours, the methyl lithium was transferred back off of the sample and a 50:1 mixture of tetrahydrofuran and concentrated aqueous HCl was transferred onto the sample by canula. At this point the sample was removed from the cuvette, rinsed with water, and dried.

Evidence that the C adsorbates are indeed present on the Si(111) surface as alkyl groups has been obtained in separate work.[9] Briefly, valence band photoemission spectra for several alkyl monolayers on silicon, including the *n*-pentyl and methyl monolayers discussed here, showed the same splitting patterns of the C 2*s*-based molecular orbitals as the parent alkanes. Moreover, Fourier transform infrared (FTIR) spectra of the *n*-pentyl and higher alkyl monolayers show the expected C–H stretching vibrations.[2]

Figure 1(a) shows the conventional x-ray photoelectron spectra of the monolayer formed from 1-pentene and H–Si(111). The inset shows the C 1*s* narrow-scan spectrum and its decomposition into two components. Fits using various C 1*s* line shapes gave ratios of the areas of the components ranging from 90%:10% to 84%:16%. The larger component with a binding energy near 285.5 eV is assigned to the emission from aliphatic carbon bonded only to hydrogen and other carbon atoms. The weaker component has a binding energy near 284.5 eV. This shift to lower binding energy by about 1 eV indicates that the carbon atom responsible for that component is bonded to an element more electropositive than carbon. Because silicon is the only element present in the sample that is more electropositive than carbon, we assign the weaker, chemically shifted component to the carbon atom of the adsorbate that is directly bonded to the silicon