Effects of the Local Environment on Si−H Stretching Frequencies for the Mixed Coverage X/H:Si(111) Surface (X = F, Cl, Br, and I)

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The vibrational spectra of the Si(111)-(1 × 1) surface covered with a mixture of halides and hydrogen are explored using computational techniques with experimental validation. We have investigated the relationship between the Si−H stretching mode and halide coverage for fluorine, chlorine, bromine, and iodine. Our investigation shows that the blue shift of the ν(Si−H) mode is approximately linear with respect to the halide coverage. Our predictions using density functional calculations are validated using experimental results on a ∼30% fluorinated surface. The origin of the shift is proposed to be an inductive effect along with lone pair donation from the halogen to the silicon surface. Our results indicate it is possible to use the ν(Si−H) mode as a probe to measure halide coverage. Our results agree with earlier studies on analogous systems.

I. Introduction

Silicon is a critically important material that is widely used by the semiconductor industry.[1,2] While most semiconductor devices currently use the Si(100) surface due to the existing technological infrastructure, the Si(111) surface has also received considerable attention. The unit cell of the unpassivated Si(111) surface in vacuum is complex with a 7 × 7 reconstruction. When an oxidized surface is etched in ammonium fluoride, the surface is terminated with hydrogen giving a remarkably simple 1 × 1 unreconstructed surface.[3] This nearly atomically flat surface is an ideal starting point for uniform functionalization. The current paradigm for semiconductor manufacturing may reach its limit around the year 2020.[4,5] Leading up to this eventuality, new innovations in designing novel functionalized surfaces are clearly important. These surfaces, which can be functionalized with organic species, can drive the technology toward organic molecular-scale electronics. Many of these reactions use the halogenated silicon surface as a starting point.[6−8] Therefore, it is important to understand the halogenated silicon surface and the halogenation process to advance fundamental science in this area.

Recently, there has been interest in functionalizing the Si(111) surface using organic molecules to explore the development of new devices.[4,9−30] One of the techniques used to achieve functionalization is a surface Grignard reaction which was first attempted in 1996[15] but has received renewed interest in the past few years.[9,10,15,22,23,31−34] In this technique, halide is substituted for the hydrogen to create a X/Si(111) (X = F, Cl, Br, and I).[20,22,23,33,35−39] Subsequently, the surface is alkylated by creating a silicon−carbon bond using the Grignard reagent. During the initial halide substitution there is a mixed coverage surface, partially covered with hydrogen and partially covered with a halogen. This surface can be used to answer two important questions. First, is it possible to track the percent coverage of the halide on the surface? Second, what is the effect of varying number of neighboring hydrogen and halide atoms

on surface structure and vibrational frequencies? Both questions rest upon the idea that the neighboring groups can exert a measurable influence one another. The effects can be probed directly using surface vibrational spectroscopy to measure the adsorbate stretching frequencies .[40,41] The use of electronic structure theory makes it possible to examine the structural changes occurring at various percentages of halide and hydrogen coverage.

Recent reports have examined these questions using either electronic structure calculations[42] or a combination of electronic structure calculations and surface vibrational spectroscopy[43] for mixed chlorinated/hydrogen Si(111) surfaces. These studies show that neighboring chlorines shift the surface vibrational frequencies by polarizing the silicon-adsorbate bond. The effect is nearly linear with coverage giving an indication that it is possible to determine the coverage using the surface vibrational shifts during the reaction. In this report we have sought to extend these results for the group 17 elements (F, Cl, Br, and I). Using electronic structure calculations we consider the shift in vibrational frequency versus coverage for the silicon-adsorbate and discuss the origin of the shifts. These results are compared to the experimental frequencies for the partial coverage (∼30%) of fluorine. We then draw some general conclusions about the mixed coverage hydrogen/halogen surfaces.

II. Methods

a. Computational Details. Functionalized Si(111) surface were modeled using periodic boundary conditions. Unit cells were constructed by choosing the smallest repeating group of the bulk crystal which replicated the proper surface geometry of the two-dimensional slab. The Si(111) surface is relatively simple allowing for a single unique atom per surface layer. To obtain models suitable for mixed coverage the single unit cell models were replicated once along each translation vector to create a four unit cell model, Figure 1. Overall the unit cell contains Si_{4n} silicon atoms with n equal to the number of layers. Due to the lack of strain on Si(111) surface termination, we have previously seen that as few as four layers are sufficient to give reliable results. As a consequence of symmetry, the number of layers must be an even integer to maintain upper and lower

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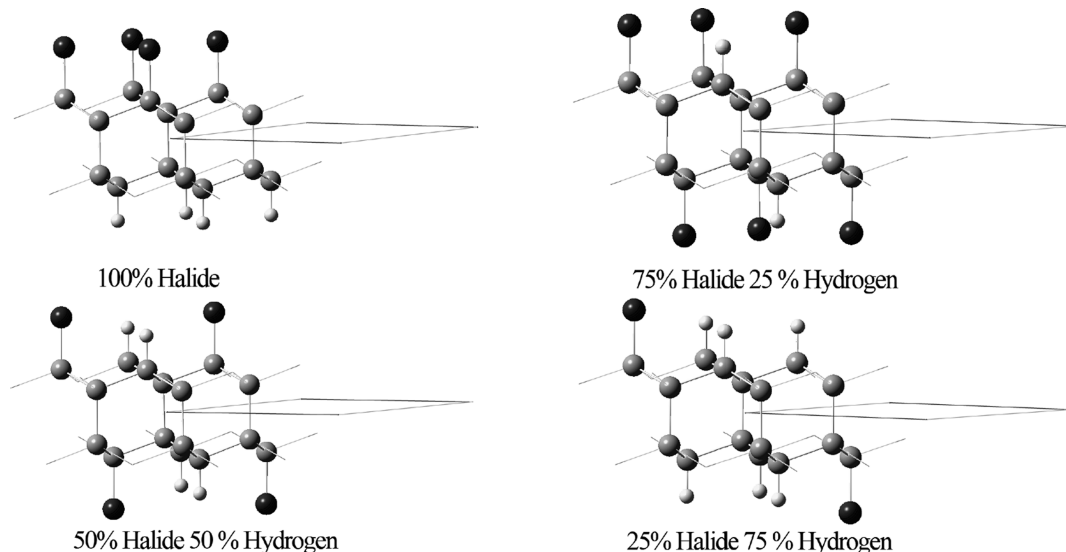*J. Phys. Chem. C, Vol. 114, No. 41, 2010* **17645**

Figure 1. Ball and stick model of the four-site PBC models used for the study. Large dark spheres represent the halides, large lighter spheres represent the silicon surface, and small spheres represent hydrogen atoms. The lines show the translation vectors.

surfaces (that need not be identical). In cases of uniform coverage, one surface is terminated with hydrogen while the opposite side is terminated with a halide. In cases of mixed coverage we have mirrored the upper and lower surfaces. Using these models it is possible to have halide coverage percentages of 0, 25, 50, and 75% (while the remainder of the surface is terminated with hydrogen).

We have used the gradient-corrected BLYP density functional (B88 exchange functional with the Lee, Yang, and Parr correlation functional) along with the Pople-style 6-31G(d,p) basis set (BLYP/6-31G(d,p) model chemistry) to investigate all the systems in this study with the exception of Iodine.[44−48] Iodine was modeled using the Los Alamos National Laboratory double-ζ basis set with added polarization functions and an effective core potential (BLYP/LANL2DZdp ECP model chemistry).[49−51] This exact, or a similar, model chemistry has been used in several previous studies on periodic systems.[52−54] Although other popular hybrid functionals such as B3LYP are more widely used, we have not seen a significant difference in previous studies.[52−54] A notable difference is the Si−Si bond distance which is known to be systematically too long by 0.04 Å with the BLYP/6-31G(d,p) model chemistry.[52,53] However, the BLYP functional is substantially more economical for PBC calculations that were performed using the implementation of Kudin et al.[55,56]

Currently the use of analytic force constants is not yet widely implemented for PBC in most popular quantum chemical programs. To obtain PBC force constants at the Γ-point (wave vector $k = 0$), we have used numerical second derivatives as in our previous studies. The analytic forces were numerically differentiated in Cartesian space (step size of 0.001 Å) using the symmetric finite difference method. The force constants were mass weighted, diagonalized, and scaled to give vibrational frequencies (scaled eigenvalues of the force constant matrix) and the normal modes (the corresponding eigenvectors). While this method does not compute the phonon dispersions, it has been sufficient to assign infrared spectra for a number of similar systems.[52−54] All calculations were done with a modified version of the GAUSSIAN development suite of programs.[57]

b. Experimental Details. Anhydrous methanol (CH₃OH) (99.8%) and anhydrous ethanol (99.5%) D (Sigma Aldrich) were placed as received inside a N₂(g)-purged glovebox prior to use.

Aqueous ammonium fluoride (40% by weight) and aqueous hydrofluoric acid (49% by weight) were obtained from J.T. Baker. Aqueous hydrogen peroxide (30% by weight) and concentrated (18 M) sulfuric acid were obtained from EM Science. Ultra pure water was provided by a Millipore station, resistivity of 18.2 MΩ cm at 25 °C.

i. Surface Preparation. The silicon samples were cut from [111]-oriented double-side polished silicon wafers. The samples were initially cleaned in "piranha", a 3:1 mixture of concentrated H₂SO₄ (98%) and H₂O₂ (30%) and copiously rinsed with ultra pure water. Silicon samples were hydrogen-terminated by a 30 s immersion in 10−20 wt % HF(aq), followed by a 2.5 min immersion in 40 wt % NH₄F(aq), and a final rinse in DIW for 10 s to obtain an atomically flat, monohydride-terminated Si(111).

ii. Methoxy and Ethoxy Termination. Reactions of H−Si(111) surfaces with liquid anhydrous methanol (or ethanol) at 65 °C for 12 h were performed as recently published.[32,41,58]

iii. Fluoride, Hydroxy, and Remethoxy Terminations. Methoxy-terminated surfaces were converted to fluoride-terminated surface by immersion of the surfaces into a Teflon beaker containing N₂(g)-purging 49 wt % HF(aq) for 3 min; the solution was purged with N₂(g) for ~45 min prior to use. The beaker was covered with a polystyrene Petri dish to minimize the amount of dissolved O₂(g), which is known to roughen the Si surface.

A HO-terminated surface was formed by placing a F-terminated surface in a covered Teflon beaker containing N₂(g)-purged DI water; the beaker was typically purged with N₂(g) for at least 45 min prior to immersion of the silicon sample. After reaction, the sample was removed from the H₂O at an angle so that it came out mostly dry; any remaining water was dried under a stream of N₂(g). F- or HO-terminated surfaces were capped under N₂(g) in 50 mL plastic centrifuge tubes, carried to the FTIR spectrometer, and situated in the N₂(g) purging bench of the spectrometer typically within 2 min.[41]

III. Results and Discussion

a. Geometric Parameters. The geometries for the functionalized Si(111) surfaces we have studied are straightforward. The distance between top layer surface atoms is ~4 Å. This distance easily permits the formation of a complete monolayer for all
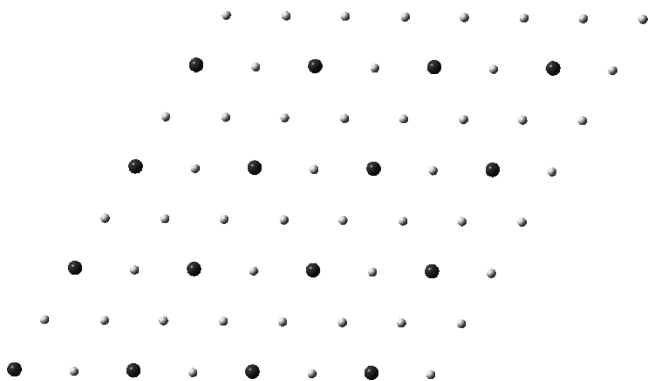
Figure 2. Top down view of the adsorbate pattern on the surface showing the *cm* wallpaper symmetry group. The large dark spheres are the halide atoms and the smaller spheres are the hydrogen atoms.

TABLE 1: Si−H Bond Lengths, Å, at Several Percentages of Halide Coverage for Fluorine, Chlorine, Bromine, and Iodine Adsorbates on the Si(111) Surface

halide	Si−H bond lengths, Å			
	0% halide	25% halide	50% halide	75% halide
fluorine	1.506	1.504	1.501	1.499
chlorine	1.506	1.502	1.498	1.496
bromine	1.506	1.501	1.498	1.495
iodine	1.506	1.501	1.497	1.495

the uniform and mixed adsorbates considered in this study. The largest adsorbate is iodine with a van der Waals radius of 1.98 Å.[59] The bonds formed by all the single atom adsorbates are normal to the plane of the surface. Therefore, when considering the surface adsorbate geometries there is only one significant parameter for the uniform surfaces and three for the mixed coverage surfaces. The uniform adsorbate parameter is the silicon-adsorbate distance. The parameters for the mixed coverage surface consist of the two silicon-adsorbate distances along with the wallpaper symmetry group that contains information about the periodic arrangements at each surface site.

Uniform adsorbates present the simplest case. The Si−H bond length is 1.506 Å and the Si-X bond distances are 1.647 Å for X = F, 2.110 Å for X = Cl, and 2.259 Å for X = Br (X = I was not calculated). The distances are all slightly longer than the corresponding values observed with small molecules (H₃SiX, X = H, F, Cl, Br, and I) using the same model chemistry by ∼0.01 Å showing an effect of the surface on the silicon-adsorbate distance. The wallpaper symmetry gives an indication of the long-range adsorbate order of the surface. The uniform adsorbates transform as the symmetry of the surface, i.e., local C_{3v} symmetry at each adsorbate site. The wallpaper symmetry is *p6m* if the lower layer silicon atoms are ignored.[60] While the uniform adsorbate case is simple, the wallpaper symmetry is important for mixed-coverage adsorbates (vide infra).

Using a model with four possible surface sites, there are three possible percentages of partial halide coverage, 25, 50 and 75%. The model of the surface with 25% halide coverage contains three hydrogens and one halide. At 50% there are two hydrogens and two halides and at 75% coverage there is one hydrogen among three halides. While these surfaces are simple, understanding the key geometrical parameters of the surface is critical to the vibrational shifts.

The 25% halide coverage has two important distance parameters, the Si−X (X = F, Cl, Br, and I) and Si−H bond distances. The local symmetry at each site is reduced to the C_{2v} symmetry group. Ignoring the lower layers silicon atoms the wallpaper symmetry is *cm*. If we consider the extended system shown in Figure 2 the surface symmetry group forms a pattern consisting of solid rows of hydrogen and a second row with alternating hydrogen and halide. This structure is the inverse of the 75% halide coverage with the same symmetry group. It is worth noting that using a four-site model the different arrangements of the adsorbates all form the same wallpaper space group and are equivalent by symmetry.

The Si-X bond distances at 25% halide coverage are 1.660 Å for X = F, 2.144 Å for X = Cl, 2.287 Å for X = Br, and

2.543 Å for X = I. The corresponding bond length-differences from the surfaces with complete termination are 0.013 Å for the fluorine, 0.034 Å for chlorine and 0.028 Å for the bromine adsorbate. The difference shows the effect of adding halides to the surface on the Si−X bond distance. The reasons for bond length shifts due to surface interactions have been previously examined in detail.[52,61−65] Three possible sources of the difference are crowding of the adsorbates, an inductive effect, and an effect via interaction of the adsorbate lone pairs with the silicon-surface bonds. The adsorbate−adsorbate distances are larger than the sum of the van der Waals radii for all of the adsorbates and the bonds lengths of the adsorbates are uniform. If the effect is due to increased crowding of the adsorbates, it is likely that additional geometrical relaxations such as unequal bond lengths or tilting of the adsorbates away from each other will be seen. The inductive effect would affect the bond lengths but would die off going down the period from fluorine to iodine. The effect of a lone pair, on the other hand, would increase down the period as polarizability increases. Our analysis suggests that the effect is due to a combination of both an inductive effect and an interaction of the lone pair of the adsorbate with the surface (vide infra). The intensity of the effects move in opposition to one another (inductive effect decreases down the period while the lone pair effect increases down the period) but both decrease the Si−X bond length. It is worth noting these interactions are fairly weak resulting in a slight shift of the bond distance.

The Si−H bond distances at 25% halide coverage show a clear trend. As shown in Table 1 the bond lengths decrease from the complete hydrogen coverage. The largest shift is for iodine and bromine where the Si−H bond distance changes from 1.506 Å to 1.495 Å. A similar pattern is observed for the other adsorbates. The origins of these bond length changes and their implications on the silicon−hydrogen stretching frequencies are discussed below.

At 75% halide coverage the symmetry group is the same as for 25% coverage. The bond lengths are considerably different. The Si−X bond lengths are longer than for the case of 25% coverage. The values for the Si−X bond lengths are 1.651 Å for X = F, 2.119 Å for X = Cl, 2.266 Å for X = Br, and 2.510 Å for X = I. The magnitude of the bond length changes are consistent with the effects discussed above. Changes to the Si−H bond lengths are shown in Table 1 and also follow the pattern discussed above for 25% coverage.

The final set contains an equal amount of halide and hydrogen adsorbates. The wallpaper space group for this surface ignoring the lower layer silicon atoms is *p2*. The extended surface has alternating rows of hydrogens and halides. Other arrangements of halides and hydrogen on the surface give the same wallpaper symmetry group. The bond distances for the Si−X bond lengths are intermediate between those of 25% coverage and 75% coverage, 1.655 Å for X = F, 2.130 Å for X = Cl, 2.275 Å for X = Br, and 2.523 Å for X = I. The Si−H bond lengths, shown in Table 1, have the pattern that would be expected from the values at other percentages of halide coverage.

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TABLE 2: Si−X (X = F and Cl) Stretching Frequency (cm⁻¹) at Different Percentages of Halide Coverage on the Si(111) Surface, the Remaining Sites Being Terminated by Hydrogen

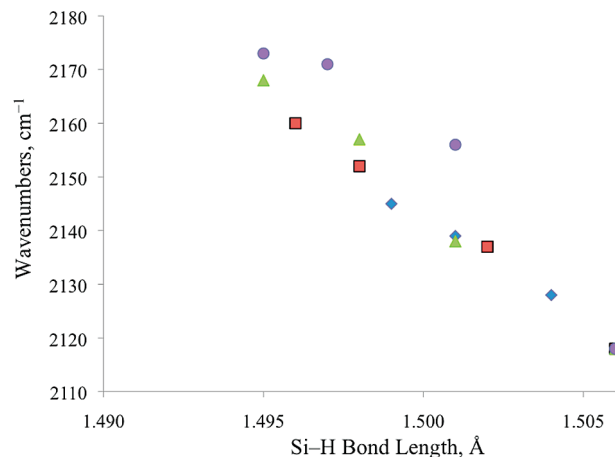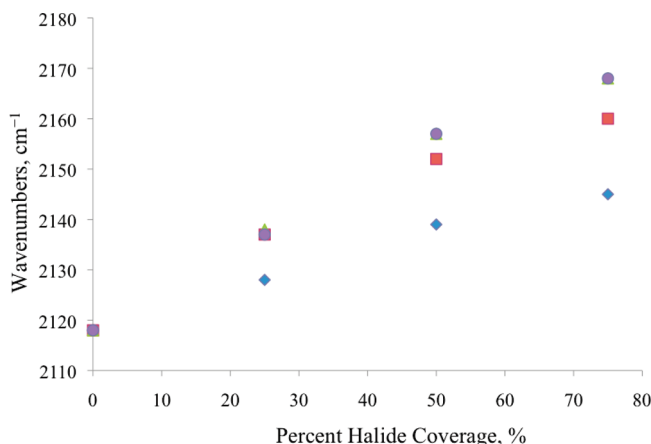|	Si−X stretching frequency, cm^{-1}			
mode	100% halide	75% halide	50% halide	25% halide
Si−F	861	843	825	807
Si−Cl	554	537	514	499

TABLE 3: The Si−H Stretching Frequency, cm⁻¹ for the Four Halides at Different Percentages of Halide Coverage on the Si(111) Surface

	Si−H stretching frequency, cm^{-1}			
halide	0% halide	25% halide	50% halide	75% halide
fluorine	2118	2128	2139	2145
chlorine	2118	2137	2152	2160
bromine	2118	2138	2157	2168
iodine	2118	2137	2157	2168

b. Vibrational Frequencies. The vibrational spectra of surfaces with uniform coverage are the simplest to consider and offer a reference for comparison. If only modes involving the adsorbate are considered, these spectra have a single perpendicular-polarized mode that is the silicon-adsorbate stretching mode. The values for the Si−X stretching frequencies (X = F, Cl, Br, and I) are shown in Table 2 and the Si−H stretching frequency in Table 3. The silicon−halide stretching frequencies are shifted higher than for the corresponding substituted silanes. The bond lengths for the surface atoms are correspondingly shorter than in the substituted silanes. The surface silicon−hydrogen stretching frequency is lower than that of silane (D₃Si−H isotopic substituted form to avoid vibrational coupling) with a longer bond length. These results show a slight stabilizing effect of the surface for the silicon-halide bond and a slight destabilizing effect for the silicon−hydrogen bond. The experimental frequencies for the hydrogen and chlorine covered surface have been reported.[43] We have previously compared these values to our computed results[43] and shown very good agreement. While there is a slight overestimation of the stretching modes by ∼30 cm⁻¹, this is expected since the frequencies were calculated using the harmonic approximation. The good agreement for the H/Cl system gives confidence to the reliability of the computed results for the fluorine, bromine, and iodine species, which have, to our knowledge, not been well studied experimentally.

The vibrational spectra of the mixed coverage surfaces are more interesting. There are significant shifts of the Si−X (X = F, Cl, Br, and I) and Si−H vibrational frequencies as the percentage of halide coverage on the surface changes. If we first examine the Si−X stretching frequencies on the H/Si(111) with varying concentrations of halide, the Si−X stretching frequencies decrease with decreasing halide coverage, Table 2. This change in stretching frequencies is approximately linear with respect to coverage for fluorine and chlorine. The stretching frequencies for bromine and iodine are well below 500 cm⁻¹ and can couple strongly to the phonons making assignment of these modes very difficult. We have, therefore, correlated the stretching frequencies to the bond lengths, which shift in the same manner as the clearly assignable chlorine and fluorine stretching frequencies.

While it is possible to experimentally characterize a Si−F and Si−Cl stretches on the Si(111) surface it is difficult to experimentally characterize larger halides. Recently, it has been proposed to use the silicon−hydrogen stretching frequency to

Figure 3. Si−H bond lengths in Å plotted against the Si−H stretching frequency in cm⁻¹. The bond lengths and frequency have a linear relationship when considering only one halide, showing a slight dependence on the local environment, fluorine (♦), chlorine (■), bromine (▲), and iodine (●).

Figure 4. Si−H stretching frequencies in cm⁻¹ plotted against the percentage of halide coverage, fluorine (♦), chlorine (■), bromine (▲), and iodine (●).

monitor the halide coverage on the surface.[30,43] Thus it is important to calibrate the relationship of the silicon−hydrogen stretching shifts with the surface coverage for the different halides.

The silicon−hydrogen stretching frequencies increase by tens of wavenumbers with the increase in halide coverage that is reflected in the bond length changes discussed previously. The relationship between the Si−H bond length and frequency is approximately linear, Figure 3. There is a slight dependence on the local environment of the hydrogen which slightly affects the slope of the bond length versus frequency relationship that has been previously noted.[43]

If the effects of particular halides are considered, several trends emerge. Fist considering partial fluorine and partial hydrogen termination, it can be seen from Figure 4 that the Si−H stretching frequencies increase linearly with increasing fluoride coverage from 2118−2145 cm⁻¹ over a range or 27 cm⁻¹. This rate of increase is the smallest for all of the halides calculated. The chlorine surface shows a similar increase in frequency. However, the rate of increase is larger than for fluorine and occurs over a larger range, 2118−2160 cm⁻¹. Under close inspection, the frequencies level off slightly, possibly indicating a saturation of the effects which are driving the frequency increase. This tapering off is also seen with bromine
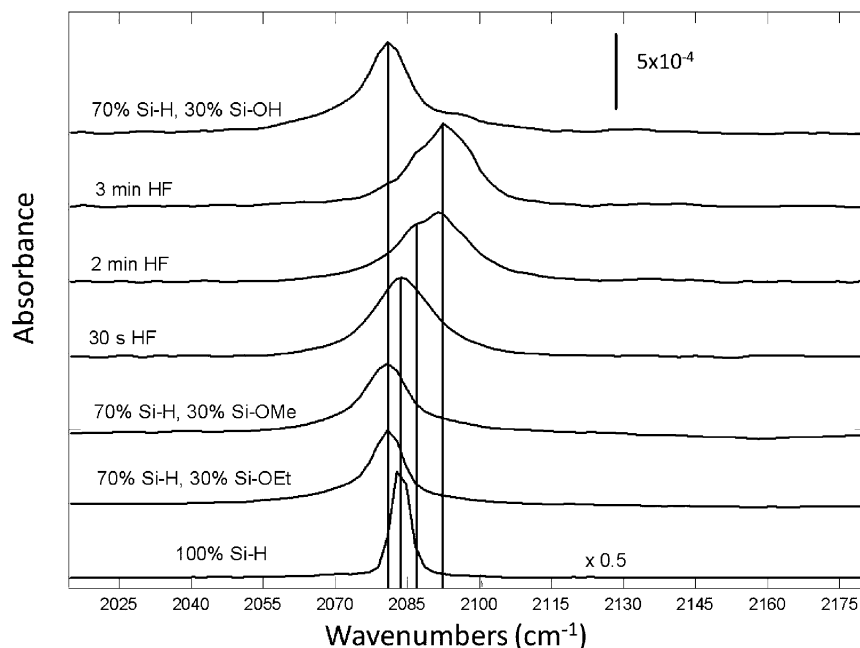
Figure 5. Transmission infrared spectra of flat silicon surfaces referenced to oxidized silicon surfaces. From bottom to top: Freshly hydrogenated silicon, after reaction with ethanol (leading to 70% SiH and 30% SiOC$_2$H$_3$) and methanol (leading to 70% Si−H and 30% SiOCH$_3$). After sequential treatment in 49% HF(aq) for t = 30, 120, and 180 s (leading to 70% Si−H and 30% Si−F), and after immersion in water (leading to 70% Si−H and 30% Si−OH).

which increases at a slightly higher rate than chlorine (2118−2168 cm^{-1}). Finally iodine shows nearly the exact same trend as bromine. The rate of increase has been previously characterized for chlorinated surface by our group[43] and by Juarez et al.[30]

The origin of the frequency shift has been proposed to be an inductive effect for the chlorinated surface.[43] When the trend for all halides is examined, it is clear that an inductive effect alone is insufficient to explain the trend. The inductive effect would increase the frequency as previously described but would be strongest for fluorine and drop off for less electronegative halides. Since the blue shift in Si−H stretching increases for less electronegative halides and is largest for bromine and iodine, another property is partly responsible for the increase in the Si−H frequency in addition to electronegativity. As the halides' size increases they become more polarizable. This increase in polarizability results in the possibility of halide lone pairs donating electron density into the surface. This donation strengthens the silicon-halide bond while slightly destabilizing the surface silicon−silicon bonds. Indirectly this allows a stronger interaction with the silicon-adsorbates, slightly strengthening the Si−H bond and increasing the frequency. The lone pair effect combined with the inductive effect, previously described,[43] significantly affects the frequencies. The inductive effect is linear with coverage and is expected to be highest for fluorine (Pauling electronegativity of 3.98) and will decrease down the period to iodine (Pauling electronegativity of 2.66). The lone pair donation is nonlinear. The lone pair effect is expected to have a large initial effect and then reach saturation quickly as halide coverage increases. This effect is highest for bromine and iodine, which are the most polarizable, and decreases up the period. The frequency shift of fluorine is likely to be almost entirely an inductive effect and shows a linear increase with coverage. The shift of bromine and iodine are likely to have a substantial contribution from the lone pair effect. In order to probe slightly deeper into the lone pair effect we have performed calculations on halide substituted trisilanes (XSiD$_2$SiD$_2$SiD$_2$H) substituted with deuterium to eliminate

hydrogen coupling. These small molecules follow the same pattern observed for the surface between different halides.

In our previous work it was difficult to calibrate the method using experimentally known percentages of halide coverage.[43] Instead, we were able to track the increase in halide Si−H stretching frequencies at specific time interval exposures to chlorine precursors.[43]

Wet chemistry on atomically smooth H−Si(111) surface has been performed to investigate the influence of atoms bonded to the neighboring silicons on Si−H stretching frequencies. Figure 5 shows the transmission FTIR spectra in the Si−H stretching region for the silicon surface at several steps of the modification process, referenced to the initial oxidized silicon. Exposing the atomically smooth H−Si(111) surface to solutions of neat anhydrous methanol or ethanol at 65 °C leads to the replacement of approximately 30% of the initial Si−H (determined by the integration of the Si−H stretching band) by Si−OCH$_3$ or Si−OC$_2$H$_5$, respectively. In both cases, complete monolayer termination is not possible due to the steric interactions between the relatively bulky surface methoxy and ethoxy groups.

The Si−H stretching mode is shifted from the initial frequency (2083 cm^{-1}) to a lower value (2079 cm^{-1}) due to average reduction of the Si−H dipole−dipole interactions.[66] The -OCH$_3$ group can then be replaced with fluorine to form a silicon−fluorine bond by immersion of the methoxy-terminated surface in HF(aq) solution. Figure 5 shows the effect of the progressive exchange of the methoxy groups by the fluorine atoms on a flat Si−H surface with ∼30% Si−OCH$_3$ coverage. The frequencies shift discretely from 2079 cm^{-1} prior to HF immersion to 2084, 2087, and 2092 cm^{-1} after 30, 120, and 180 s HF immersion in HF, corresponding to the replacement of the methoxy-terminated surface with fluorine atoms. The final blue shift of the Si−H on the ∼30% Si−F surface is 13 cm^{-1}. The calculated results indicate that at 30% coverage the Si−H blue shift should be 11 cm^{-1}. This remarkable agreement shows the robust nature of the relationship between halide coverage and frequency. When fluorine atoms are replaced by hydroxyl
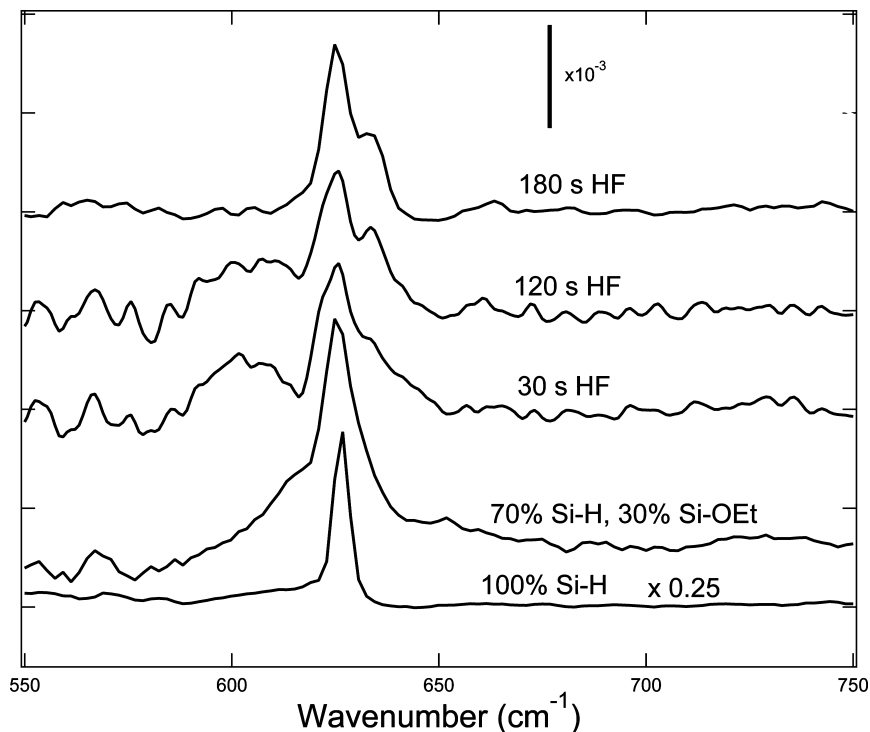
Figure 6. Transmission IR-spectra silicon surfaces referenced to oxidized silicon surfaces showing the region typically associated with the Si−H bending modes. From bottom to top: 100% hydrogenated silicon, after 30% −OCH$_3$ coverage, after sequential treatment in 49% HF(aq) for t = 30, 120, and 180 s (leading to 30% Si−F coverage).

groups by immersion into water, the Si−H stretching frequencies red shift again to the same position as that of the flat Si−H surface with ∼30% Si−OCH$_3$ or Si−OC$_2$H$_5$ coverage.

It is interesting that the methoxy surface does not show a shift due to lone pair donation. Oxygen does contain lone pairs that should shift the spectra in a similar manner as the halides. Using methoxy functionalized trisilanes it is possible to understand why this may be the case. By choosing the trisilanes which best reproduce the geometry of the surface and calculating the frequencies of the trans and gauche geometries, one can calculate the splitting due to orientation of the methoxy group. In the trans configuration, when the lone pairs of the oxygens point toward the hydrogen of interest, the lone pair donation of the oxygen strengthens the Si−H bond (1.487 Å), increasing the frequency. If the lone pair of the oxygen is oriented away from the hydrogen of interest, the bond is weakened (1.490 Å), decreasing the frequency. This clearly shows a lone-pair effect due to the hydroxyl (or methoxy) group on a neighboring Si−H bond. The key to understanding why this is not present on the surface is to carefully consider the surface geometry. On the surface there are two equivalent orientations of the methoxy groups. In both orientations, a methoxy group lone pair will face toward some hydrogen and away from others. Therefore, the effect is nearly canceled by both positive and negative frequency shifts from neighboring methoxy groups. An effect of this type is not possible for halides, which are spherical.

In previous studies, the Si−H bending modes were observed not to shift after 30% coverage of −OCH$_3$. Upon fluorination of the surface a shoulder is observed in the region of the Si−H bending mode, Figure 6. The most likely attribution of this feature is a split in the bending modes due to the lower symmetry of the 30% Si−F surface. The experimental splitting for the peaks is ∼17 cm^{-1}. The calculated vibrational modes show splitting for the bending modes but the lack of calculated intensites for these modes makes it difficult to make definitive

assignments. The splitting of the calculated Si−H bending vibrations for the 50% fluorine/50% hydrogen coverage is approximately 15 cm^{-1} for analogous modes. The splitting is due to the lower symmetry of the system that makes the surface directions nonequivalent. However, the close agreement is probably fortuitous since the coverage in the calculations is not the same as in the experiments. It is interesting that a similar splitting of 15−22 cm^{-1} is calculated for the other halogenated surfaces. More work is necessary to completely understand the dependence of the splitting on the adsorbate coverage.

IV. Conclusions

We have investigated the geometries and frequencies of the Si(111)-1 × 1 surface with mixed halide and hydrogen coverage. We have further characterized the relationship between the ν(Si−H) mode and the percentage of halide coverage. The ν(Si−H) mode blue shifts with increasing halide coverage. The relationship is linear for fluorine and approximately linear for chlorine and bromine. Iodine is increasingly nonlinear as a function of increased coverage. At high surface site coverage, chlorine, bromine and iodine show saturation of the effects. The calculated values were calibrated by experimentally characterizing a ∼30% fluorine surface which showed outstanding agreement with the predicted values. Our proposed explanation for the origin of the shifts is a combination of an inductive effect, which is highest for fluorine and declines down the period, along with a lone pair donation to the silicon surface which is highest for bromine and iodine and decreases up the period.

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