# First Principles Investigation of HCl, H<sub>2</sub>, and Chlorosilane Adsorption on Cu<sub>3</sub>Si Surfaces with Applications for Polysilicon Production

Shwetank Yadav<sup>†</sup><sup>®</sup> and Chandra Veer Singh<sup>\*,†,‡</sup><sup>®</sup>

<sup>†</sup>Department of Materials Science and Engineering and <sup>‡</sup>Department of Mechanical and Industrial Engineering, University of Toronto, Toronto M5S 3E4, Canada

**Supporting Information** 

**ABSTRACT:** The hydrochlorination reaction used in polysilicon production is often catalyzed through copper-based materials which have been found to form the Cu<sub>3</sub>Si intermetallic under reaction conditions. The structure and composition of the  $\eta''$  phase, present in the reaction temperature range, has been only recently derived. We conduct the first study of Cu<sub>3</sub>Si surfaces and their interaction with molecules. Two surfaces of the  $\eta''$  phase were examined through density functional theory, a silicon-rich Si termination



in hexagonal geometry and an equal-parts copper and silicon CuSi termination in honeycomb geometry. The adsorption of  $H_{2}$ , HCl,  $SiCl_2$ , dichlorosilane ( $SiH_2Cl_2$  or DCS), trichlorosilane ( $SiHCl_3$  or TCS), and silicon tetrachloride ( $SiCl_4$  or STC) was tested on multiple sites. The SiCu termination favorably adsorbed only the  $SiCl_2$  molecule, where a bridge position between a Cu and Si atom produced the strongest adsorption. The Si-terminated surface dissociatively adsorbed HCl at all sites with almost equal adsorption energies. The  $SiCl_2$  adsorbed at all sites but greatly preferred a Cu–Si bridge site, where it produced the strongest adsorption of this study. The  $H_2$  molecule moved away from the surface for all sites. The STC molecule was unfavorable at sites with closely spaced Cu and Si atoms but dissociatively adsorbed at the other sites with more isolated Si atoms. The TCS molecule underwent dissociative chemisorption on all sites while the DCS molecule moved away from the surface for all site types. Therefore, the Si-terminated surface is preferred for molecular adsorption and appears to provide promising starting sites for surface hydrochlorination reactions.

### INTRODUCTION

High purity silicon is essential for the production of both microelectronics and photovoltaic (PV) solar cells. The strong recent growth in PV deployment and high expected future growth<sup>1</sup> has resulted in increased research focus on the manufacture of solar grade silicon in order to decrease costs and improve output. Metallurgical grade silicon (MG-Si), which has been obtained after ore processing, is typically further refined into solar grade silicon through chemical processes in a number of energy-intensive steps.

The majority of the world's solar grade silicon is produced by the Siemens process or its variants.<sup>2</sup> This involves chemical vapor deposition of high purity silicon from trichlorosilane (SiHCl<sub>3</sub> or TCS), where TCS is itself initially made from MG-Si. The entire process also produces large amounts of silicon tetrachloride (SiCl<sub>4</sub> or STC) as a byproduct. This excess STC can be converted back into useful TCS through two main routes. The first involves hydrogenation of STC in a hightemperature (greater than 1373 K) gas phase reaction

$$SiCl_4(g) + H_2(g) \rightarrow SiHCl_3(g) + HCl(g)$$
 (1)

The second lower temperature route, known as hydrochlorination, makes use of MG-Si (and hence can be conducted in the first stage of the Siemens process)

$$Si(s) + 3SiCl_4(g) + H_2(g) \rightarrow 4SiHCl_3(g) + HCl(g)$$
(2)

This reaction is traditionally thought to occur in two steps, the gas phase reaction 1 above followed by a surface reaction

$$Si(s) + 3HCl(g) \rightarrow SiHCl_3(g) + H_2(g)$$
(3)

The reacting system is similar for both hydrochlorination and vapor deposition for the polysilicon process, and there is still no consensus about the complex reactions which can occur, especially with regard to gas—solid interactions. Dozens of elementary reactions and compounds involving the Si, Cl, C, and H atoms have been proposed to be present in the gas phase for this system.<sup>2</sup> Theoretical first principles-based computational studies have taken the lead in such investigations as these techniques can easily study reactions which are difficult to isolate experimentally and are present in low proportion or consist of transient or fast reacting species.

Most papers on gas phase reactions used quantum chemistry Gaussian-*n* composite methods involving Møller–Plesset perturbation theory and transition state or canonical variational transition state theory. These studies dealt with various

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decomposition reactions of silanes and chlorosilanes or their reactions with Cl, H, or  $H_2$  and often obtained reaction activation barriers.<sup>3-16</sup>

There are very few ab initio studies looking at gas–surface interactions and surface reactions for the Siemens process. Because of the more expensive nature of modeling surfaces, these studies used density functional theory (DFT) but with atomic orbital basis sets which approximate surfaces as clusters of atoms and using hybrid functionals. These studies mostly dealt with adsorption, desorption, and surface diffusion of H<sub>2</sub>, HCl, or SiCl<sub>2</sub>.<sup>17–20</sup>

The hydrochlorination reactions have limited STC conversion when conducted with plain Si, especially below 873 K. One of the primary methods of increasing STC conversion has been through catalyst addition, with copper-based materials being the most widely used and studied. These catalysts also have the advantage of achieving these conversions at lower operating temperatures, taking place at temperatures of 723–873 K. Ding et al.<sup>21</sup> looked at Cu, CuO, and CuCl as possible hydrochlorination reaction promoters. All species were found to exhibit an advantage in STC conversion (compared to MG-Si alone) only when well mixed with silicon particles.

The best conversion was provided by CuCl, followed by CuO and then Cu. The CuO underwent reduction through  $H_{2}$ , and CuCl reacted directly with Si to both produce Cu. This Cu then reacts with Si to form the Cu<sub>3</sub>Si intermetallic, which was observed to occur for each catalyst sample using X-ray powder diffraction (XRD) techniques. The presence of Cu<sub>3</sub>Si produced after the addition of CuCl in a hydrochlorination process was also confirmed by Qing-yuan et al.<sup>22</sup> The Cu<sub>3</sub>Si alloy has also long been regarded as playing a catalytic role in the hydrogenation of methylchlorides as part of the Rochow process. The intermetallic further shows up during the copper alloying purification of MG-Si,<sup>23</sup> which might then be subjected to the hydrochlorination process for further refining. Hence, the interaction of the Cu<sub>3</sub>Si surface with gas molecules and its potential catalytic properties are of great interest.

In a follow-up study, Ding et al.<sup>24</sup> suggested a catalytic mechanism where CuCl first forms Cu<sub>3</sub>Si regions on Si particle surfaces after heat treatment; STC subsequently adsorbs and participates in surface reactions which produce TCS while using up surface silicon in the process. The Cu-Si bond was thought to play a critical role in these surface reactions. Hence, Si serves as both catalyst and reactant source. The fast diffusion of Cu atoms in silicon continually renews the Cu<sub>3</sub>Si phase along the edges of the expanding reacted region (with the pure Si regions showing negligible activity). The continual presence of Cu<sub>3</sub>Si was confirmed by XRD throughout the reaction sampling over 60 h of operation. However, scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX) analysis of the reactive regions (characterized by pits on the surface) showed a Cu/Si atomic ratio of 1.67 just after heat treatment and a ratio of roughly 1 after reactions started, suggesting that the surface atomic distribution might be more complex than that of bulk Cu<sub>3</sub>Si.

The structure of Cu<sub>3</sub>Si itself can be quite complex with several possible polymorphs, whose atomic scale structure is still being studied and not fully defined. There are six reported phases in the literature so far:  $\eta'''$  for temperatures below 573 K,  $\eta''$  between 573 and 743 K,  $\eta'$  between 743 and 830 K, and three phases of  $\eta$  at high temperature. However, complete structure and composition information is not known for most of these phases. The most complete crystal structure of  $\eta'$  Cu<sub>3</sub>Si was proposed by Palatinus et al.<sup>25</sup> but without full knowledge of chemical atomic composition of each atomic site. More recently, Corrêa et al.<sup>26</sup> conducted a detailed investigation of  $\eta''$  and discovered the  $\eta'''$  phase, obtaining atomic structure and chemical composition information for the first time. They found the two phases to have very similar modulated structures with slight variations in symmetry due to atomic placement.

The typical catalyst operating temperatures for hydrochlorination fall within the stability ranges of the  $\eta''$  and  $\eta'$ phases, and hence, the structure provided by Corrêa et al. is of interest for studying this system. The average structure of the  $\eta''$  system unit cell was described as being formed from stacking of four symmetry independent types of layers: with one layer being Si-rich, one being split between Si and Cu, and two being Cu-rich. On the basis of the similarity of the  $\eta''$  and  $\eta'$  phases, that paper's authors (some of whom were co-authors in the Palatinus et al.<sup>25</sup> paper from the same research group) were confident that the phase transition from  $\eta''$  to  $\eta'$  is an order-disorder transition. This involves the Cu-Si layer now having a random distribution of atoms instead of an alternating order but retains the same structure. Hence, the provided  $\eta'$ structure should serve well as a model for both phases of interest.

Previous studies for the hydrochlorination reaction on silicon surface have been conducted using clusters which do not simulate continuous surfaces and may not be able to capture the long range effects of a crystalline structure. Plane-wave-based DFT is ideally suited for such a task as it simulates periodic slabs with unbroken surfaces and can handle larger numbers of atoms. This study aimed to look at the interaction of  $H_2$ , HCl, SiCl<sub>2</sub>, dichlorosilane (SiH<sub>2</sub>Cl<sub>2</sub> or DCS), STC, and TCS with the Cu<sub>3</sub>Si surface using a periodic slab model. This will allow for determination of the most favorable adsorption sites and binding energies and is an important step toward determining reaction kinetics and mechanisms. We believe this to be the first published ab initio atomistic simulation of Cu<sub>3</sub>Si surfaces or their interaction with any molecules.

### METHODOLOGY

The simulations were performed using plane-wave-based DFT as implemented in the Quantum ESPRESSO software.<sup>27</sup> Interactions between the valence electrons and the ionic core were represented by the projector augmented wave<sup>28</sup> method with Perdew–Burke–Ernzerhof formulation.<sup>29</sup> Kinetic energy cutoffs of 680 eV (50 Ry) and 3400 eV (250 Ry) were used for the wave functions and the charge density, respectively. Brillouin zone integrations were performed using a Monkhorst–Pack<sup>30</sup> grid of  $2 \times 2 \times 1$  k-points for initial surface structure determination and then  $\gamma$  point only for surface molecule interaction. All calculations were non-spin-polarized. A vacuum layer of 15 Å was added to avoid interaction between periodic surface images. The structures were relaxed using a Davidson minimization algorithm until the magnitude of the residual Hellman-Feynman force on each atom was less than 0.025 eV Å<sup>-1</sup>.

The adsorption (or binding) energy of a molecule on the surface was calculated as

$$\Delta E_{\rm ads} = E_{\rm tot} - E_{\rm bare} - E_{\rm ad} \tag{4}$$

where  $E_{tot}(E_{bare})$  is the energy of the slab with (without) adsorbate and  $E_{ad}$  is the energy of the isolated adsorbate species calculated in the same supercell. Hence, a negative



**Figure 1.** Average  $\eta''$ -Cu<sub>3</sub>Si bulk structure as viewed along the *c* unit cell axis. The unit cell is contained within the two solid red lines. There are four symmetry independent types of layers: a Si-only hexagonal layer (A), a Cu-only honeycomb geometry layer (B), a Cu-only hexagonal layer (C), and a Cu and Si honeycomb layer with both atom species alternating in 1:1 composition ratio (D). These layers are stacked in a sequence (ABCDCBABCDCB) along the [001] direction to form a 12-layer unit cell. The planes along which the bulk structure was cleaved to form surfaces are shown by the dotted red lines, forming a Si-terminated surface (along layer A) and a CuSi- terminated surface (along layer D). The PDOS of the bulk material is shown on the right, showing a degree of electron sharing between Cu and Si. Blue atoms represent Si, while brown atoms represent Cu.



**Figure 2.** Relaxed CuSi-terminated surface (a) top view with supercell boundaries (four supercells pictured). The surface layer with all atoms below blacked out is shown in (b), more clearly showing the honeycomb geometry with alternating Cu and Si atoms in a 1:1 ratio. The side view of the slab is shown in (c). The charge density is shown in (d), with a [110] purple plane inserted to intersect the top layer atoms to highlight the exposed surface charge. PDOS is shown in (e), showing a metallic character.

 $\Delta E_{\rm ads}$  indicates stable adsorption, whereas a positive value indicates unstable adsorption, with a more negative value

indicating more favorable adsorption. Zero-point energy corrections and Helmholtz free energies were calculated

using the harmonic limit model as implemented in the atomic simulation environment software package.<sup>31</sup>

# ■ CU<sub>3</sub>SI STRUCTURE

The unit cell of the average  $\eta''$ -Cu<sub>3</sub>Si structure derived by Corrêa et al.<sup>26</sup> was found to consist of four symmetry independent types of layers: a Si-only hexagonal layer (A), a Cu-only honeycomb geometry layer (B), a Cu-only hexagonal layer (C), and a Cu and Si honeycomb layer with both atom species alternating in 1:1 composition ratio (D). These layers are stacked in a sequence (ABCDCBABCDCB) along the [001] direction to form a 12-layer unit cell in the supercell approximation. Figure 1 shows this unit cell when viewed along the *c* unit cell axis. On the basis of the similarity of the  $\eta''$  and  $\eta'$  phases, the authors predict that the phase transition from  $\eta''$ to  $\eta'$  (whose atomic structure was derived by Palatinus et al. but where the chemical composition of each site was not certain) is an order-disorder transition where the atoms in layer D are now randomly distributed instead of having an alternating placement (but still retaining the 1:1 composition ratio). Hence, the provided  $\eta''$  structure should serve well as a model for both  $\eta''$  and  $\eta'$  phases, which are present in the catalytic hydrochlorination temperature range.

The modulated nature of the structure, taking place mostly in layer B, led to partial occupancies for that layer in the provided structure. For all such closely spaced positions which overlapped, a single atomic position was randomly chosen. As this takes place in a Cu-rich layer and the position differences are minute, it is not anticipated to have any effect on surface chemical reactivity. As only two of the independent layers contain Si and the purpose of hydrochlorination is to form TCS from surface Si, only layers A and D are of interest as surfaces. The lattice parameters we obtained after cell relaxation (a = 16.392 A, c = 43.949 A) closely matched the experimentally derived cell parameters (a = 16.245 A, c =44.017 A) of Corrêa et al.<sup>26</sup> The partial density of states (PDOS) of the bulk structure is also shown, with the overlap of Cu and Si orbitals indicating strong covalent bonding and sharing of electrons.

## CUSI-TERMINATED SURFACE

The CuSi surface unit cell is shown in Figure 2, where its symmetric honeycomb geometry is clearly visible. Because of the alternating order of Cu and Si atom placement in the top layer, there are only three unique sites for adsorption: one over a Cu atom, one over a Si atom, and a bridge position between a Cu and Si atom. The distance between the surface layer and the layer below decreased slightly from the bulk structure as the system minimized surface energy during relaxation. The system itself was modeled using a 5-layer slab, with the bottom three layers fixed to simulate effect of the bulk structure.

Our previous study for adsorption on the Si(100) surface<sup>32</sup> showed that HCl and SiCl<sub>2</sub> have the strongest adsorption energies, thought to be due to the polarized and undercoordinated natures of each respectively. The SiCl<sub>2</sub> molecule is investigated as it is regarded as an intermediate species in many theorized mechanisms for the hydrochlorination reaction and is easier to form from surface Si(s) atoms. Therefore, both these molecules were first tested before attempting the generally less reactive other molecules.

The results are shown in Table 1. Surprisingly, the HCl molecule did not have a negative binding energy for any site,

Table 1. Adsorption Energies (eV) for HCl and SiCl<sub>2</sub> Molecules on the CuSi-Terminated Surface

site	HCl	SiCl <sub>2</sub>
Si	0.26	-0.62
Cu	0.25	-0.79
bridge	0.25	-0.90

consistently moving away from the surface during relaxation. The HCl molecule, which was initially placed parallel to the surface, also always oriented itself vertically with the H atom closer to the surface. This provides a hint that there might be a region of negative charge over the atoms at the surface and that there is not much uneven charge distribution on the surface which could interact with polarized molecules. This is possibly present due to electron sharing regions which distribute charge almost equally around the hexagon rings of the honeycomb geometry, as is seen in graphene<sup>33</sup> which has the same honeycomb structure. This would also seem to be confirmed by the charge density shown in Figure 2d. The metallic-like nature of the PDOS (Figure 2e) also indicates extensive electron sharing.

The SiCl<sub>2</sub> molecule did undergo reasonable adsorption through weak chemisorption. For the Si site, the molecule adsorbed directly over the atom as seen in Figure 3a, with Si atom moving slightly upward out of the surface plane. For the bridge site, producing the strongest adsorption, the molecule formed bonds with the neighboring Cu and Si atoms as seen in Figure 3b, with both atoms rising slightly out of the top surface plane. The PDOS for the bridge site (Figure 3c) confirms the covalent type chemisorption bonding through overlap of peaks of each species. Similarly, the charge density difference (Figure 3d) charge gain in the bonds between the SiCl<sub>2</sub> Si and surface atoms, also indicates charge sharing and covalent bonding. For the Cu site, the molecule eventually relaxed to a bridge-type configuration as well. The H<sub>2</sub> and STC molecules did not adsorb in such a weakly interacting environment as expected, with both actively moving away from the surface upon relaxation and producing positive binding energies. Hence, the STC and DCS molecules were not tested for the surface.

#### SI-TERMINATED SURFACE

The Si-terminated surface after structural relaxation is shown in Figure 4. Each surface Si atom is surrounded by five (or six for the Si atom in the bottom left of the supercell) Cu atoms, which are mostly in the layer below. These Cu atoms are at varying distances from the top layer and some are even at the same level as the Si atoms. The Cu atoms were originally all in a more or less uniform plane in the layer below prior to relaxation. Similarly, the Si atoms were in a hexagonal arrangement with triangular tiling when cleaved from the bulk structure. Figure 5 shows the effects of the surface reconstruction after relaxation, where the Cu atoms are no longer in a planar uniform layer but have moved up into the top layer to varying degrees while the Si atoms of the top layer have also moved down toward the lower layers. The charge density of the surface layer (Figure 4e) shows a more uneven distribution of charge in comparison to the CuSi surface and has several isolated regions of charge which might better interact with adsorbates. The PDOS also has sharp peaks above the Fermi level for Cu, indicating highly localized electron distribution, and the surface shows a semi-metallic-like peak distribution.



Figure 3. Adsorption of SiCl<sub>2</sub> over a (a) Si atom site and (b) bridge site as seen from the top and side of the slab. The bond angle of the molecule for (a) is 107.9°, which decreases to 105.8° for (b). The PDOS (c) and charge density difference (d) of the bridge site show the covalent nature of the bonding. Blue atoms represent Si and yellow atoms represent Cl, while brown atoms represent Cu. For (d), yellow represents regions of charge gain, while blue represents regions of charge loss.

The resulting surface has reduced symmetry and four types of Si atom sites for adsorption (see Figure 4b): site 1 corresponds to Si atoms bonded to five Cu atoms in the layer below with no adjacent Si atoms (there is at least a Cu atom in the lower layer between any neighboring Si atoms), site 2 corresponds to two Si atoms with an adjacent Si atom and a Cu surface atom bonded to both, site 3 corresponds to a Si atom with an adjacent Si atom and a surface Cu bonded only to the first Si atom, and site 4 corresponds to a Si atom bonded to six C atoms in the lower layer. Note that the closeness and almost merging of the top two layers could be regarded as a mixed Cu–Si surface when examined by experimental equipment and could still qualify as the system observed through SEM–EDX by Ding et al.<sup>24</sup>

As initial tests of HCl and SiCl<sub>2</sub> proved promising, all six molecules were tested for adsorption and the results are shown in Table 2. The most favorable binding site for each molecule then had its Helmholtz free energy of adsorption calculated at 300 K in order to consider zero-point energy and temperature effects. Every adsorption attempt resulted in negative potential binding energies; though after corrections, the free energies for  $H_2$  and DCS turned positive. The HCl molecule adsorbed strongly for each site, all of whom provided very similar adsorption energies. The mechanism was through dissociation of the molecule and each atom migrating to form a bond with a surface Si atom as shown in Figure 6a for site 1. The  $H_2$  molecule had surprisingly weak interaction with the surface, again with similar values for all sites, and the molecule actually moved away from the surface in each case to a distance of roughly 3 Å. The slightly positive free energy confirms that the molecule prefers to stay away from the surface.

The adsorption of  $SiCl_2$  proved to be strong but varied based on the site. For sites 1 and 4, the molecule directly adsorbed over the Si atom as shown in Figure 6b for site 1. For sites 2 and 3, with adjacent Cu atoms in the surface layer, the molecule shifted to occupy a bridge position between a Si atom and its adjacent Cu atom and formed bonds with both atoms as seen in Figure 6c. This bridge configuration also produced the strongest adsorption of the tested molecules.



Figure 4. Relaxed Si-terminated surface (a) top view with supercell boundaries (one supercell pictured). The surface layer with all atoms below blacked out is shown in (b) along with sites tested for molecular adsorption. Note that some Cu atoms have become part of the surface layer. Side views of the slab are shown in (c) with only top layer highlighted in (d). The charge density is shown in (e), with a [110] purple plane inserted to intersect the top layer atoms to highlight the exposed surface charge. PDOS is shown in (f), showing the more localized electron distribution and semi-metallic nature of this surface compared to the Cu–Si surface.



**Figure 5.** Reconstruction of the Si surface from its initial bulk positions. The bulk positions on the left, obtained after cleavage along the silicon containing layer A (see Figure 1), clearly show the hexagonal geometry (with triangular tiling) of the silicon atoms, which are in a distinct layer separate from the layer below. The relaxed positions on the right show that the distance between the Si layer and the layer below has decreased with some Cu atoms becoming part of the top layer, and a distinct boundary between the two layers is not apparent.

The STC molecule also had varying adsorption strength with site and the most varied configurations. For sites 2 and 3, the molecule actually moved away from the surface while still producing an overall negative adsorption energy similar to the  $H_2$  molecule but was even further away from the surface at 4 Å. On the other hand, for sites 1 and 4, the molecule adsorbed strongly and dissociated into Cl and SiCl<sub>3</sub>. Each dissociated part migrated to adsorb over a Si atom, with the SiCl<sub>3</sub> cluster

Table 2. Molecular Adsorption Energies (eV) on the Si-Terminated Surface  $\!\!\!^a$ 

site	HCl	$H_2$	SiCl <sub>2</sub>	STC	TCS	DCS
1	-1.89	-0.21	-1.12	-1.33	-1.28	-0.26
2	-1.87	-0.22	-2.18	-0.27	-1.25	-0.28
3	-1.83	-0.21	-2.09	-0.25		
4	-1.90	-0.22	-1.20	-1.34		
$\Delta F$	-1.67	0.14	-2.43	-1.57	-1.11	0.31

"Sites are labeled according to locations shown in Figure 4. All adsorption tests resulted in a more stable system, although all sites for  $H_2$ , sites 2 & 3 for STC, and all sites for DCS had the molecule not staying at the surface but moving slightly away from it. The Helmholtz free energy for the most favorable site for each species at 300 K is also listed.

bonding through its Si atom with the Cl atoms facing away from the surface as can be seen in Figure 7. The charge density difference (b) shows movement of charge into interatomic bond regions and indicates strong covalent bonding. Similarly, the PDOS (c) shows a smoothing out of Cu atom peaks above the Fermi level compared to the bare surface in Figure 4f, indicating a more delocalized sharing of electrons in covalent bonding. The TCS and DCS molecules did not show much variance between sites 1 and 2, the two sites most different in their geometry, and so were not tested for other sites. The TCS molecule dissociatively adsorbed for both sites with a slightly weaker energy than STC on site 1. The DCS molecule did not dissociate and had fairly weak negative potential



Figure 6. Dissociative adsorption of (a) HCl at site 1, (b)  $SiCl_2$  on site 1, and (c)  $SiCl_2$  on site 3 for the Si-terminated surface as seen from the top and side of the slab. Red atoms represent hydrogen.

binding energies and a slightly positive free binding energy, ending up at distances of around 4 Å or greater from the surface to the central Si atom.

The increased reactivity of the Si-terminated surface in comparison to the CuSi-terminated surface is likely due to the more uneven surface geometry of the former. The surface atoms of the Si-terminated surface are almost all bonded to atoms which are in a lower layer, and are not bonded to any adjacent atoms in the same layer (with the exception of atoms at sites 2 and 3, which are only bonded to one or two other atoms in the same layer but still have most of their bonds to lower layer atoms). This results in these surface atoms being more exposed with larger relative gaps to the other surface atoms. It should be noted that the adsorption of SiCl<sub>2</sub> and STC becomes more favorable with temperature effects while that of HCl and TCS slightly decreases.

In contrast, the CuSi-terminated surface has each surface atom bonded to three other surface atoms in the same layer, forming a uniform charge distribution as discussed in the earlier section. This leaves each atom far less exposed to approach from an adsorbate molecule, both due to smaller distance between adjacent surface atoms and less regions of reduced charge around each atom. The more favorable Siterminated surface itself has varied sites, which can be more favorable for different kinds of molecules (sites 1 & 4 are preferred by STC while sites 2 & 3 are preferred by SiCl<sub>2</sub>). This further seems to confirm that the Si surface is most favorable for carrying out surface reactions and is preferred to promote such reactions. The Si-terminated surface also produced adsorption following the same trends as those of the Si(100) surface of our earlier study<sup>32</sup> in terms of which molecules had stronger binding energies. The binding energies were weaker than for the Si(100) surface for all molecules except SiCl<sub>2</sub> which had similar binding energies.

## PROPOSED TCS FORMATION MECHANISM

The defining feature of the hydrochlorination reaction is the consumption of silicon from the solid surface to produce gas phase TCS. The removal of the Si atom from the solid phase is



**Figure 7.** Dissociative adsorption of STC at site 1 of the Si-terminated surface (a), as seen from the top and side of the slab. The charge density difference (b) and PDOS (c) are also shown. For (b), yellow represents regions of charge gain, while blue represents regions of charge loss.

the most likely energetically challenging step. Hence, this likely proceeds through an intermediate species, for which  $SiCl_2$  is a prime candidate and which can then react further with surfaceadsorbed Cl and H atoms to produce TCS. The H and Cl required for  $SiCl_2$  and TCS would be supplied from HCl dissociative adsorption and diffusion of the resulting atoms. Hence, a possible reaction mechanism occurs through the following set of elementary steps and reaction energies

$$HCl(g) + * \to Cl^* + H^*$$
 ( $\Delta E = -1.90 \text{ eV}$ ) (5)

$$2\mathrm{Cl}^* + \mathrm{Si}(\mathrm{s}) \to \mathrm{Si}\mathrm{Cl}_2^* \qquad (\Delta E = 0.94 \text{ eV}) \tag{6}$$

$$\operatorname{SiCl}_{2}^{*} + \operatorname{Cl}^{*} + \operatorname{H}^{*} \to \operatorname{SiHCl}_{3}(g) \qquad (\Delta E = 0.10 \text{ eV})$$
(7)

# CURRENT CHALLENGES AND FUTURE RESEARCH DIRECTIONS

This study looked at the preliminary adsorption of some important reactant molecules for the hydrochlorination reaction. The natural progression is to then look at elementary

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processes and their activation barriers, such as those for adsorbing  $H_2$  as well as surface reactions. Specifically, the formation of SiCl<sub>2</sub> from surface silicon is of interest as well as any other mechanisms which result in silicon etching of the surface. This should hopefully provide insight into the catalytic nature of the Cu–Si bond and its advantages over the plain silicon surface. Similar studies can also be conducted for other materials theorized to have catalytic effects for this system, such as iron, nickel, and cobalt. Another follow-up should be conducted with simulations which take into account coverage, temperature, and other entropic effects through techniques such as ab initio molecular dynamics and kinetic Monte Carlo.

## CONCLUSIONS

This paper looked at the surface of  $\eta''$ -Cu<sub>3</sub>Si, using a recently derived structure and chemical composition model, to study the hydrochlorination reaction for polysilicon production when taking place in copper-catalyst-promoted systems. The adsorption of H<sub>2</sub>, HCl, SiCl<sub>2</sub>, dichlorosilane (SiH<sub>2</sub>Cl<sub>2</sub> or DCS), trichlorosilane (SiHCl<sub>3</sub> or TCS), and silicon tetrachloride (SiCl<sub>4</sub> or STC) was tested on two surface terminations; the Si-terminated surface formed from a silicon-only hexagonal geometry layer of the bulk structure and a CuSi termination formed from a honeycomb geometry layer of the bulk structure with alternating Cu and Si atoms. The CuSi termination was found to weakly chemisorb the SiCl<sub>2</sub> molecule, with a bridge site between Cu and Si atoms the most favorable. However, none of the other molecules adsorbed favorably on this termination, with all of them moving away from the surface during relaxation.

The Si-terminated surface was found to reconstruct upon relaxation to have a less symmetric arrangement of surface Si atoms. The distance between the top layer and the underlying Cu-only layer decreased until they almost merged and some Cu atoms moved up into the surface layer. The HCl molecule strongly adsorbed through dissociative chemisorption over all the sites tested, with each atom of the molecule bonding to surface Si atoms. The H<sub>2</sub> molecule moved away from the surface for each site.

The SiCl<sub>2</sub> molecule also strongly adsorbed over all sites of the Cu termination, but for sites with adjacent Cu and Si surface atoms it adsorbed in a bridge position and produced the strongest adsorption energies of the study. The STC molecule on the other hand moved away from the surface for such adjacent Cu and Si atom sites in a manner similar to the H<sub>2</sub> molecule. However, for other sites with isolated Si atoms, the STC molecule underwent strong adsorption through dissociative chemisorption. The TCS molecule underwent dissociative chemisorption for both isolated Si atom sites and those with adjacent Si and Cu atoms. The DCS molecule on the other hand moved away from the surface for both kinds of sites.

Our results suggest that the Si-terminated surface is preferred to carry out surface reactions because of its uneven geometry with exposed Si atoms, whereas the uniformly distributed geometry and charge of the CuSi-terminated surface make it almost inert to molecular adsorption.

### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b04460.

Molecular adsorption configurations for most favorable site of each molecule not depicted in main text, including adsorption of SiCl<sub>2</sub> placed over a Cu atom site on the CuSi-terminated surface and adsorption of TCS placed over site 1 and adsorption of H<sub>2</sub> and DCS placed over site 2 on the Si-terminated surface (PDF)

#### AUTHOR INFORMATION

#### Corresponding Author

\*E-mail: chandraveer.singh@utoronto.ca.

#### ORCID 🔍

Shwetank Yadav: 0000-0001-8816-121X

Chandra Veer Singh: 0000-0002-6644-0178

#### Notes

The authors declare no competing financial interest.

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# REFERENCES

(1) Pandey, A. K.; Tyagi, V. V.; Selvaraj, J. A. L.; Rahim, N. A.; Tyagi, S. K. Recent advances in solar photovoltaic systems for emerging trends and advanced applications. *Renewable Sustainable Energy Rev.* **2016**, *53*, 859–884.

(2) Yadav, S.; Chattopadhyay, K.; Singh, C. V. Solar grade silicon production: A review of kinetic, thermodynamic and fluid dynamics based continuum scale modeling. *Renewable Sustainable Energy Rev.* 2017, 78, 1288–1314.

(3) Su, M. D.; Schlegel, H. B. An ab initio MO study of the thermal decomposition of chlorinated monosilanes, SiH4-nCln (n = 0-4). J. Phys. Chem. **1993**, 97, 9981–9985.

(4) Wittbrodt, J. M.; Bernhard Schlegel, H. An ab initio study of the thermal decomposition of dichlorosilane. *Chem. Phys. Lett.* **1997**, *265*, 527–531.

(5) Swihart, M. T.; Carr, R. W. Thermochemistry and Thermal Decomposition of the Chlorinated Disilanes (Si2HnCl6-n,n= 0–6) Studied by ab Initio Molecular Orbital Methods. *J. Phys. Chem. A* **1997**, *101*, 7434–7445.

(6) Swihart, M. T.; Carr, R. W. On the mechanism of homogeneous decomposition of the chlorinated silanes. Chain reactions propagated by divalent silicon species. *J. Phys. Chem. A* **1998**, *102*, 1542–1549.

(7) Zhang, Q.; Wang, S.; Gu, Y. Direct ab Initio Dynamics Studies of the Reactions of H with SiH4-nCln(n=1-3). *J. Phys. Chem. A* **2002**, 106, 3796–3803.

(8) Pei, K.; Li, H. Ab initio and kinetic calculations for the reactions of Cl with SiHnCl4-n (n=1,2,3,4). *J. Chem. Phys.* **2004**, *121*, 6738–6742.

(9) Zhang, X.; Ding, Y.-h.; Li, Z.-s.; Huang, X.-r.; Sun, C.-c. Ab initio study on the rate constants of SiCl4 +  $H \rightarrow$ SiCl3 + HCl. *Phys. Chem. Chem. Phys.* **2001**, *3*, 965–969.

(10) Walch, S. P.; Dateo, C. E. Thermal Decomposition Pathways and Rates for Silane, Chlorosilane, Dichlorosilane, and Trichlorosilane. *J. Phys. Chem. A* **2001**, *105*, 2015–2022.

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(11) Walch, S. P.; Dateo, C. E. Reactions of SiCl2and SiHCl with H and Cl Atoms. J. Phys. Chem. A 2002, 106, 2931–2934.

(12) Deng, J.; Su, K.; Wang, X.; Zeng, Q.; Cheng, L.; Xu, Y.; Zhang, L. Thermodynamics of the gas-phase reactions in chemical vapor deposition of silicon carbide with methyltrichlorosilane precursor. *Theor. Chem. Acc.* **2008**, *122*, 1–22.

(13) Ge, Y.; Gordon, M. S.; Battaglia, F.; Fox, R. O. Theoretical Study of the Pyrolysis of Methyltrichlorosilane in the Gas Phase. 3. Reaction Rate Constant Calculations. *J. Phys. Chem. A* **2010**, *114*, 2384–2392.

(14) Junko, T.; Momose, T.; Shida, T. Thermal Rate Constants for SiH4  $\rightarrow \leftarrow$  SiH3 + H and CH4  $\rightarrow \leftarrow$  CH3 + H by Canonical Variational Transition State Theory. *Bull. Chem. Soc. Jpn.* **1994**, 67, 74–85.

(15) Yu, X.; Li, S.-M.; Li, Z.-S.; Sun, C.-C. Direct Ab Initio Dynamics Studies of the Reaction Paths and Rate Constants of Hydrogen Atom with Germane and Silane. *J. Phys. Chem. A* 2000, 104, 9207–9212.

(16) Matsumoto, K.; Klippenstein, S. J.; Tonokura, K.; Koshi, M. Channel Specific Rate Constants Relevant to the Thermal Decomposition of Disilane. *J. Phys. Chem. A* **2005**, *109*, 4911–4920.

(17) Barbato, A.; Cavallotti, C. Challenges of introducing quantitative elementary reactions in multiscale models of thin film deposition. *Phys. Status Solidi B* **2010**, 247, 2127–2146.

(18) Cavallotti, C. Reactivity of silicon surfaces in the presence of adsorbed hydrogen and chlorine. *Chem. Vap. Deposition* **2010**, *16*, 329–335.

(19) Kunioshi, N.; Anzai, K.; Ushijima, H.; Fuwa, A. Effects of cluster size on calculation of activation energies of silicon surface reactions with H2 and HCl. *J. Cryst. Growth* **2015**, *418*, 115–119.

(20) Anzai, K.; Kunioshi, N.; Fuwa, A. Analysis of the dynamics of reactions of SiCl 2 at Si(100) surfaces. *Appl. Surf. Sci.* 2017, 392, 410–417.

(21) Ding, W.-J.; Yan, J.-M.; Xiao, W.-D. Hydrogenation of Silicon Tetrachloride in the Presence of Silicon: Thermodynamic and Experimental Investigation. *Ind. Eng. Chem. Res.* **2014**, *53*, 10943–10953.

(22) Qing-yuan, L. I.; Pei-long, L. I.; Tie-feng, W. Experimental Study on Hydrogenation of SiCl4 to SiHCl3 in a Stirred Bed Reactor. *Chin. J. Process Eng.* **2016**, *16*, 767.

(23) Mitrašinović, A. M.; Utigard, T. A. Refining Silicon for Solar Cell Application by Copper Alloying. *Silicon* **2009**, *1*, 239–248.

(24) Ding, W.-J.; Wang, Z.-B.; Yan, J.-M.; Xiao, W.-D. CuCl-Catalyzed Hydrogenation of Silicon Tetrachloride in the Presence of Silicon: Mechanism and Kinetic Modeling. *Ind. Eng. Chem. Res.* 2014, 53, 16725–16735.

(25) Palatinus, L.; Klementová, M.; Dřínek, V.; Jarošová, M.; Petříček, V. An Incommensurately Modulated Structure of  $\eta'$ -Phase of Cu3+xSi Determined by Quantitative Electron Diffraction Tomography. *Inorg. Chem.* **2011**, *50*, 3743–3751.

(26) Corrêa, C. A.; Perez, O.; Kopeček, J.; Brázda, P.; Klementová, M.; Palatinus, L. Crystal structures of  $\eta''$ -Cu3+x Si and  $\eta'''$ -Cu3+x Si. Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater. **2017**, 73, 767–774.

(27) Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G. L.; Cococcioni, M.; Dabo, I.; et al. QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *J. Phys.: Condens. Matter* **2009**, *21*, 395502.

(28) Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, *59*, 1758–1775.

(29) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, 77, 3865–3868.
(30) Monkhorst, H. J.; Pack, J. D. Special Points for Brillouin-Zone

Integrations. *Phys. Rev. B: Solid State* **1976**, *13*, 5188–5192. (31) Larsen, A. H.; Mortensen, J. J.; Blomqvist, J.; Castelli, I. E.; Christensen, R.; Dułak, M.; Friis, J.; Groves, M. N.; Hammer, B.; Hargus, C.; et al. The atomic simulation environment–a Python library for working with atoms. J. Phys.: Condens. Matter 2017, 29, 273002.

(32) Yadav, S.; Singh, C. V. Molecular Adsorption and Surface Reactions of HCl, H2 and Chlorosilanes on Si(100)-c(4x2) with Applications for High Purity Silicon Production. *Appl. Surf. Sci.* 2018.

(33) Yadav, S.; Zhu, Z.; Singh, C. V. Defect engineering of graphene for effective hydrogen storage. *Int. J. Hydrogen Energy* **2014**, *39*, 4981–4995.

(34) Hirel, P. Atomsk: A tool for manipulating and converting atomic data files. *Comput. Phys. Commun.* **2015**, *197*, 212–219.

(35) Momma, K.; Izumi, F. VESTA 3for three-dimensional visualization of crystal, volumetric and morphology data. J. Appl. Crystallogr. 2011, 44, 1272–1276.

(36) Kokalj, A. Computer graphics and graphical user interfaces as tools in simulations of matter at the atomic scale. *Comput. Mater. Sci.* **2003**, *28*, 155–168. Proceedings of the Symposium on Software Development for Process and Materials Design