Correlation of reaction sites during the chlorine extraction by hydrogen atom from Cl Si (100) 2 × 1

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Correlation of reaction sites during the chlorine extraction by hydrogen atom from Cl/Si(100)-2×1

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The Cl abstraction by gas-phase H atoms from a Cl-terminated Si(100) surface was investigated by scanning tunneling microscopy (STM), high-resolution core level photoemission spectroscopy, and computer simulation. The core level measurements indicate that some additional reactions occur besides the removal of Cl. The STM images show that the Cl-extracted sites disperse randomly in the initial phase of the reaction, but form small clusters as more Cl is removed, indicating a correlation between Cl-extracted sites. These results suggest that the hot-atom process may occur during the atom-adatom collision. © *2007 American Institute of Physics.*
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I. INTRODUCTION

The extraction of adsorbates on both metal and semiconductor surfaces by impinging hydrogen atoms has attracted attention as a model system for understanding the fundamental dynamics of gas-surface reactions.[1–6] One of the many model systems among these studies is the production of HCl gas species from a Cl-terminated Si(100) surface [Cl/Si(100)]. In this system, an incident H-atom flux reacts with Cl atoms adsorbed on the Si(100) surface and produces gaseous HCl molecules: $H_{(g)} + Cl_{(ad)}/Si(100) \rightarrow HCl_{(g)} + Si(100)$. This gas-surface reaction has practical applications for Cl reduction in Si atomic layer epitaxy at low temperature[7] and for the dry etching process in very large scale integration.

One of the main scientific issues behind these studies is to examine the role of three disparate surface reaction mechanisms at the gas/solid interfaces. In the idealized Langmuir-Hinshelwood (LH) mechanism, two reagents react after they have been chemisorbed and are in thermal equilibrium with the surface. Most surface reactions are believed to occur by this method. In the idealized Eley-Rideal (ER) mechanism, a direct, single gas-surface collision is responsible for the reaction between an incident gas-phase species and another adsorbed reagent. The occurrence of this pathway has been clearly demonstrated by Lykke and Kay[8] and by Rettner.[5] In the hot-atom (HA) mechanism, a trapped incident gas-phase species bounces a few times or diffuses for a short distance before reacting with another adsorbed reagent. This pathway falls between the two idealized pathways and has been shown to be the dominant reaction mechanism for the production of both H_2 and HCl in the reaction of H atoms with H- and Cl-covered metal surfaces.[2,9]

Halogen and hydrogen atoms form strong bonds on a semiconductor surface and barely diffuse at near room temperature.[10] Therefore, surface species are likely to retain their position after an extraction of halogen by an incident H atom.[11] Utilizing Auger electron spectroscopy and temperature-programmed desorption (TPD) mass spectroscopy, Cheng *et al.* found that the halogen removal rate by $H_{(g)}$ is first order in both the Cl/Br surface coverage $(\theta_{Cl}, \theta_{Br})$ and in the H flux (F_H).[12] They also reported an activation energy of 91 meV per Cl removed and concluded that the H-extraction process follows an Eley-Rideal reaction mechanism, where the surface reaction is mainly driven by the high internal energy of incident atomic hydrogen. Using time-of-flight scattering and recoiling spectroscopy to measure the real-time surface H and Br coverage, Koleske and Gates verified that the removal rate of Br on the Si(100) surfaces with H atom has a linear dependence on both θ_{Br} and F_H below 500 °C.[6] In addition to the linear dependence on θ_{Br} and F_H, the same reaction on the Si(111) surface also has a linear dependence on the hydrogen coverage θ_H, indicating a more complex kinetics. The linear dependence of the reaction rate on θ_{Br} is consistent with an ER pathway. However, the structure dependence of the reaction leads to the suggestion that the H atom may be partially accommodated at the surface in a mobile "hot precursor" state before the reaction with the adsorbed Br. From the theoretical aspect, Kim *et al.* studied the $H_{(g)} + Cl_{(ad)}/Si(100)$ system using the classical trajectory approach and concluded that all reactive events occur through a localized ER mechanism.[13]

As mentioned earlier, previous experimental studies employed various spectroscopic techniques to measure the kinetics and dynamics of the gas-surface reaction. Hattori *et al.* first investigated the fact that atomic hydrogen extracts chlorine from Si(111)-7×7 using a scanning tunneling microscope (STM).[14] The authors showed that Cl atoms are extracted from the Cl-covered Si(111) surface by atomic H, and that the surface Si atoms, after H bombardment, are terminated with H atoms. The clean Si(100) surface after Cl ter-

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mination at room temperature has a relatively simple structure: The silicon dimers retain their bonding and the surface layer consists of rows of Cl–Si–Si–Cl species.[15,16] The surface species exhibit the same dimerized structure, namely, –Si–Si–Cl, –Si–Si–, H–Si–Si–, and H–Si–Si–H after immediate Cl extraction and further H adsorption.[16,17] Taking advantage of these facts, we utilized both the synchrotron radiation photoemission spectroscope and the STM to observe the Cl/Si(100) surface in atomic resolution after H-atom exposure. By comparing the results from the measurement with those from the computer simulation, it is evident that the reaction does not occur simply as the result of a single collision with unitary reaction probability between the gas atom and the adatom.

II. EXPERIMENT

The Si(100) samples were sliced from Boron-doped wafers with a dopant concentration of approximately 1.5×10^{15} cm^{-3}. After outgassing at ~ 900 K for ~ 12 h, a dimerized clean Si(100) surface was obtained by dc Joule heating to ~ 1450 K for a few seconds. After direct heating, chlorine molecules were introduced through a leak valve and a stainless-steel tube to the sample surface at room temperature to form the Cl-terminated Si(100)-2×1 structure. A hot tungsten-spiral filament was used to produce atomic hydrogen. The filament was ~ 5 cm away from the Si(100) substrate and heated to ~ 1800 K when the chamber was backfilled for a period of time T with H$_2$ to a pressure P of about 2×10^{-7} torr without sensitivity correction. Maxwell's distribution expects the kinetic energy of the dissociated H atoms from the hot filament surface to be 0–230 meV. From the geometry of the filament and the samples, it was estimated that the incident angles of H atoms was less than $\sim 25°$ from normal. The apparent H$_2$ exposure, i.e., $P \times T$, is presumably proportional to the actual dosage of hydrogen atoms on the surfaces. The atomic hydrogen flux was not measured directly in the present study. Instead, the apparent exposure in Langmuir (1 L=10^{-6} torr s) is used as the relative measurement of H dosage on the Cl–Si(100) surface.

The photoemission spectra were observed at the Taiwan Light Source laboratory in Hsinchu, Taiwan. Synchrotron radiation from a 1.5 GeV storage ring was dispersed by a wide-range spherical grating monochromator. The photocurrent from a gold mesh positioned in the synchrotron beam path was monitored to calibrate the incident photon flux. Photoelectrons were collected 15° from the surface normal and analyzed by a 125 mm hemispherical analyzer in a μ-metal shielded UHV system. The overall energy resolution was less than 120 meV. The STM measurement was performed in a separated UHV chamber.

III. RESULTS

A. Photoemission results

High-resolution core level photoemission spectroscopy can be used to distinguish atoms at nonequivalent sites and in different chemical bonding configurations, according to shifts in their binding energy.[18] Figures 1(a) and 1(b) show the respective surface-sensitive Cl 2p and Si 2p core level
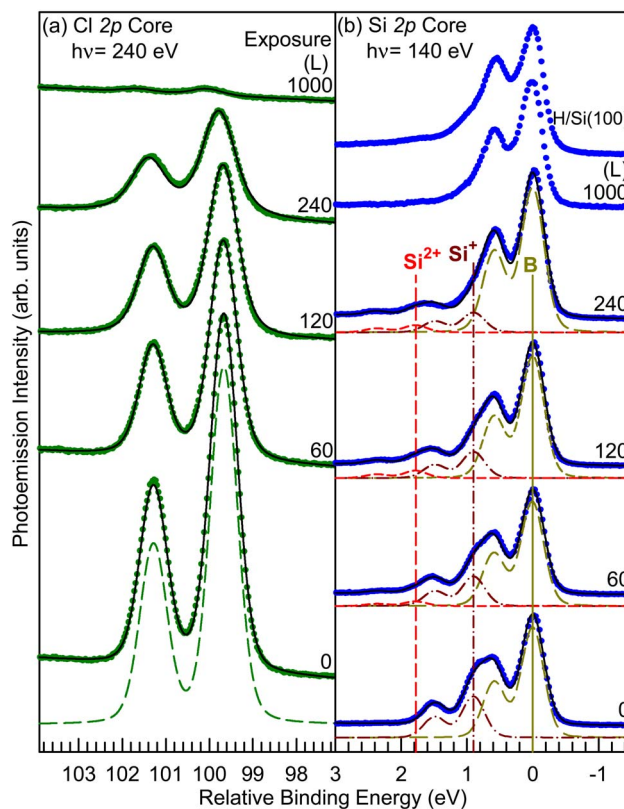

FIG. 1. (Color online) The (a) Cl 2p and (b) Si 2p core level photoemission spectra (circles) for the Cl–Si(100)-2×1 surface and the same surface after various apparent H-atom dosages as labeled. The solid curves are fits to the spectra. The curves labeled B (long dashed curves), Si$^+$ (dashed dot), and Si^{2+} (short dashed curves) are the results of decomposition of the Si 2p spectra into contributions from the bulk, Si–Cl, and Cl–Si–Cl species, respectively. The energy zero in (b) refers to the 2$p_{3/2}$ bulk position for the Cl–Si(100)-2×1 surface. To eliminate the band bending effect, the relative binding energy for the Cl 2p refers to the corresponding Si 2$p_{3/2}$ line of the B component in (b).

spectra (circles), and their decomposition into constituent components from the Cl–Si(100)-2×1 surface before and after H bombardment at 325 K for various dosages. All fitting was least-squares fitting.[19] Each component that consists of a pair of spin-orbit split doublets is assumed to have the same Voigt line shape.

The Cl 2p spectra in Fig. 1(a) can be analyzed with a component that consists of a pair of split doublets separated by 1.60 eV. The binding energy of these Cl 2p spectra relative to that of the corresponding Si 2p remains at 99.60 eV, suggesting that the Cl atoms form similar Si–Cl bonds. Figure 2 plots the integrated intensities of the Cl 2p spectra (I_{Cl}), which are proportional to the surface Cl coverage. The integrated intensity of the bottom spectrum is normalized to be 1.0 because the chlorine coverage is nominally 1 ML for the Cl-saturated Si(100) surface prior to H-atom bombardment. I_{Cl} decreases linearly with the dosage of H atoms in the early stage, indicating that Cl atoms were removed by impinging H atoms. This result is consistent with a previous study.[12]

The bottom spectrum in Fig. 1(b) shows the Si 2p core level spectra for the Cl–Si(100)-2×1 surface. This Si 2p spectrum consists of two components, B and Si$^+$, separated by about 0.9 eV. The B component is responsible for emis-
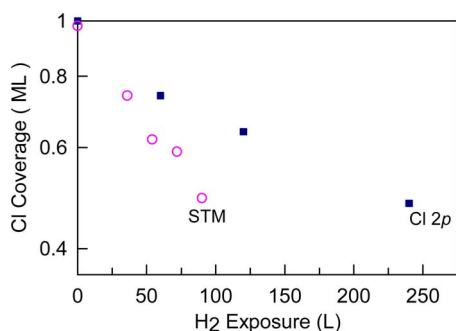
FIG. 2. (Color online) Cl coverage calculated from the integrated intensities of the Cl 2p core level spectra in Fig. 1(a) (solid squares) and from those counting from the STM images (open circles). The initial coverage is nominally 1.0 ML based on the STM result.

sion from the bulk and the Si^+ component from the surface Si–Cl species.[20] As the exposure of atomic hydrogen increases, both the intensities of the Si^+ component and the Cl 2p spectra drop off. This occurrence suggests that H atoms reduce the surface Cl coverage, similar to the findings of a previous report.[12] After >1000 L of apparent exposure, the line shape of Si 2p is similar to that [top spectrum in Fig. 1(b)] obtained by direct, high-dosage hydrogen exposure on the clean Si(100)-2×1 surface at room temperature.[21] This observation indicates that hydrogen atoms terminate nearly all surface dangling bonds and form a mixture of dihydride and monohydride surface when most Cl atoms are extracted. It should be noted that a small component labeled Si^{2+} emerges in Fig. 1(b) after H impingement. The chemical shift of Si^{2+}, around 1.78 eV on the higher bonding energy side of B, is consistent with a charged state of +2 for Si atoms and is responsible for $SiCl_2$ species.[15] Presumably, the $SiCl_2$ species were formed as a consequence of the highly exothermic uptake of halogens during the extraction. Although more study is needed, the emersion of the dichloride species implies that impinging H atoms induces other surface reactions besides extracting upon collision with a surface adatom.

B. STM results

The clean Si(100) surface consists of rows of dimers, where the two dangling bonds from the two atoms in a dimer form a weak π bond.[22] Cl adsorption on a clean Si(100) surface saturates the dimer dangling bonds while preserving the basic (2×1) dimer structure without buckling, as shown in Fig. 3(a).[23,24] In Fig. 3(a), a handful of dark sites can be discerned, each occupying one side of a Cl–Si–Si–Cl species. As Figs. 3(b) and 3(c) show, the density of these dark sites increase with the H exposure. The dangling bonds generated during the Cl removal exhibit a higher apparent height due to enhanced tunneling near the Fermi level, and they are highly reactive to further H adsorption.[25] The dark sites in Fig. 3 are H-terminated sites. The initial H coverage on the Cl/Si(100) surface is less than 0.02 ML. The presence of some initial surface H is likely due to the residue in the cleaning process and/or the adsorption of impurity by the HCl molecules in the Cl_2 gas source. The remaining Cl coverage after H exposure can be obtained by directly counting its density in the STM images. The results are plotted in Fig.
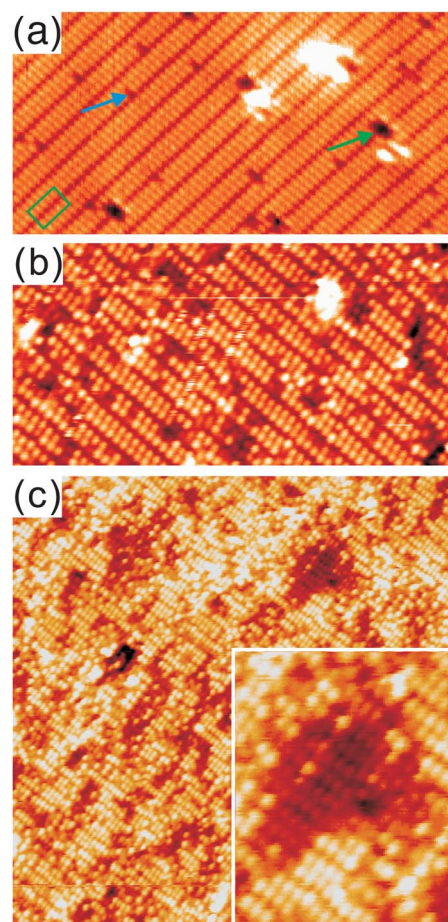

FIG. 3. (Color online) STM images of the Cl/Si(100)-2×1 surface after (a) 0, (b) 36, and (c) 90 L apparent dosages of H atoms. The sample bias used was +2 V. In (a) the green rectangle box, running from the upper right to the lower left, encloses a row of five Cl–Si–Si–Cl (monochloride) species. A surface Cl atom appears as a bright protrusion and forms a narrow ellipse with another in the neighboring monochloride row in the image. Notably each of two nearest Cl adatoms in the empty state images are not from a single Cl–Si–Si–Cl species, but are a part of two adjacent Cl–Si–Si–Cl species. The green and blue arrows point to a missing dimer defect site and a H-termination site, respectively. The inset in (c) shows a 2×1 area of nearly complete H termination after Cl extraction. The size of a 1×1 unit cell in the image is 3.84×3.84 Å².

2. Since the STM and photoemission measurements were performed in different chambers, the actual H dosages for the two measurements are different but proportional, as shown in Fig. 2.

When the substrate temperature is held at RT during H-atom exposure, a reaction site, where a Cl atom is removed by an H atom and an H atom is subsequently adsorbed, presumably undergoes no diffusion.[11,26] The brightest humps in the images are likely weakly bonded terrace $SiCl_2$ moieties, as evident from the photoemission spectra and as discussed in the previous section. In addition, the remaining Cl-terminated sites and bright humps, and most of the reacted sites in Figs. 3(b) and 3(c), appear to be H terminated. At first glance, the H-terminated sites, or the Cl-extracted sites, appear to be randomly dispersed. However, as will be analyzed and discussed in the following section, the density and the sizes of the clusters grouped together in neighboring Cl-extracted sites are larger than those created by random
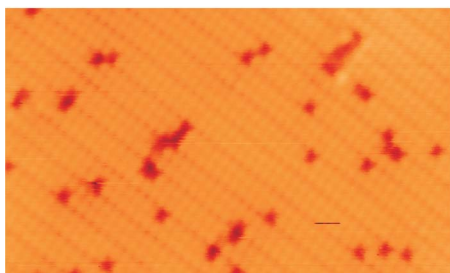
FIG. 4. (Color online) STM images of the Cl/Si(100)-2×1 surface after 12 L apparent dosages of H atoms at a sample temperature of 600 K. The sample bias used was +2 V.

extraction. At higher H-atom exposure, even two-dimensional islands with a H/Si(100)-2×1 structure, as shown in Fig. 3(c), can be easily found. Figure 4 shows an STM image for the $H_{(g)}$+$Cl_{(ad)}$/Si(100) reaction at a substrate temperature of ∼600 K. Similar isolated dark sites occupying one side of a dimer can be easily identified, since they are H-terminated sites after Cl extraction. The density of the Cl-extracted sites increases as the H-atom dosage and the clustering of reaction sites become evident at higher H-atom dosage. The results are similar to those obtained at near room temperature.

IV. DISCUSSION

In the ER mechanism, a Cl-extraction reaction occurs via a collision-induced reaction. The calculated cross section is smaller than a unit cell within a small proximity around the spot where an H atom strikes.[13] The gas-phase H atoms impinge on the surface in a random fashion. In this scenario, a new Cl-extracted site is generated no matter what neighboring chemical environment surrounds the site where an H atom strikes. In other words, the extraction probability upon collision with an H atom is not changed when a Cl–Si surface species is neighboring one or more dangling bond sites or monohydride sites. If this scenario is valid, then the distribution of the Cl-extracted sites by the random and sequential impingement of gas-phase H atoms will be completely random in the STM images.

Figures 5(a)–5(c) show the results of the impingement-site distribution from the computer simulation based on this assumption. In the simulation, a reactive site is randomly generated since the impact parameter found in the classical trajectory approach is small.[13] In Fig. 5, the Cl-extracted sites are classified into eight categories, and are marked in different colored intensity scales (labeled 0–8), according to the degree of reaction-site clustering. A site in categories numbered k=0, 1, 2, and 3 is a Cl-extracted site with 0, 1, 2, and 3 of its four nearest neighboring Cl-extracted sites (labeled s=1−4 in Fig. 6), respectively. If a Cl-extracted site with its four nearest neighboring Cl extracted is called a "surrounded site," a site in category 4, 5, 6, 7, and 8 is a surrounded site and has 0, 1, 2, 3, and 4 nearest neighboring surrounded sites, respectively. In the classification scheme, the category number k of a Cl-extracted site indicates the number of other extraction reactions occurring in its imme-
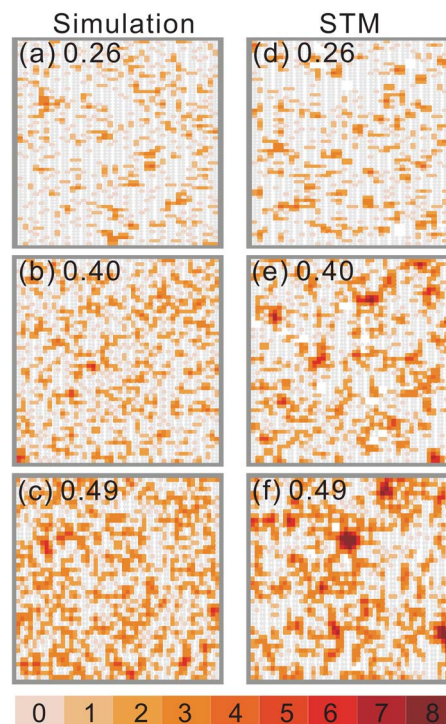

FIG. 5. (Color online) Distribution of Cl-extracted sites obtained from [(a)–(c)] simulation and [(e)–(f)] STM. The coverage of Cl-extracted sites in monolayer is labeled. The simulation starts on an area which initially consists of 50×50 Cl adatom sites. A Cl-extracted site is classified into eight categories and represented by a 1×1 cell of different colors as indicated. The "digitalized" STM images were obtained from parts of STM images typically about 30×30 nm² in size.

diate vicinity. Therefore, the larger the cluster formed by the Cl-extracted sites, the darker the cluster appears in the image.

Figure 6 displays the "unnormalized" pair distribution function (g') of Cl-extracted sites,

$$g'(s) = g(s)\theta = \frac{1}{N}\sum_{i=1}^{N}\frac{n_i(s)}{m(s)},\qquad(1)$$

where $n_i(s)$ is the number of sth-nearest-neighbor Cl-extracted sites around the ith Cl-extracted site (labeled 0 in Fig. 6), θ denotes the coverage of the Cl-extracted sites, and $m(s)$ denotes the number of sth-neighbor sites.[27] As expected, the pair distribution g' obtained from the simulated images is roughly equal to θ, independent of site index s. Figure 6 shows that g' calculated from simulation images such as Figs. 5(d)–5(f) is in agreement with those expected for a completely random distribution. In contrast, g' for nearest neighboring sites s=1−4 obtained from STM images is boosted by about 20%. g' for next nearest neighboring sites s=5−10 is also boosted at higher coverage. The deviation of g' from the mean coverage θ suggests the existence of correlation and interaction between Cl-extracted sites and, therefore, rules out the pure ER process with unitary reaction probability.[28]

To further examine whether or not the cluster formation of Cl-extracted sites results from random H impingement, STM images taken after the reaction were digitized and are shown in Figs. 5(d)–5(f) in a similar fashion to those in Figs.
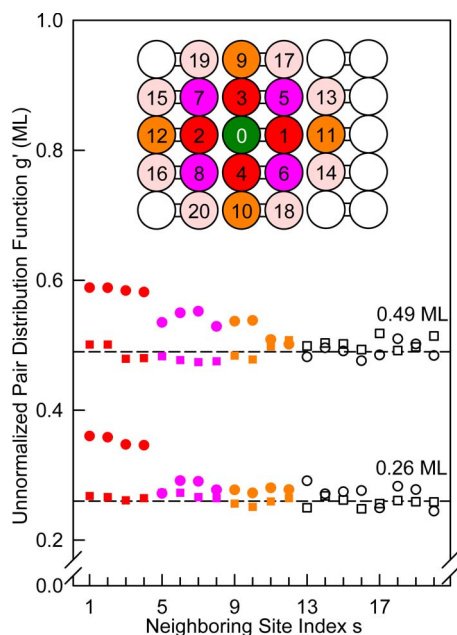
FIG. 6. (Color online) The Cl-terminated Cl–Si(100) surface and the unnormalized pair distribution function of Cl-extracted sites vs the neighboring site s obtained from a set of the STM images (circles) and the simulation (squares), and the completely random distribution calculation (dashed curves). The coverage of Cl-extracted sites in monolayer is labeled. The inset shows the Cl/Si(100)-2×1 lattice; each circle corresponds to an initial Cl adatom site. Numbers mark the respective sites around a Cl-extracted site at the center position (labeled 0). The distribution functions obtained from several STM measurements and simulations vary slightly for each s, but their overall trends are the same.

5(a)–5(c). A direct visual comparison between Figs. 5(b) and 5(e), and Figs. 5(c) and 5(f) suggests that the site population for categories with a greater k obtained from the STM measurement $[P_{STM}(k)]$ is greater than that $[P_{Sim}(k)]$ from the corresponding simulated images. Their ratios $P_{STM}(k)/P_{Sim}(k)$, plotted in Fig. 7, deviate significantly from 1.0, especially for $k>4$. This finding also indicates that the simulation based on the assumption of a pure ER process deviates from the experimental results. The cluster formation of Cl-extracted sites can only be realized if an impinging H atom "senses" the chemical environment in a small (HA) or
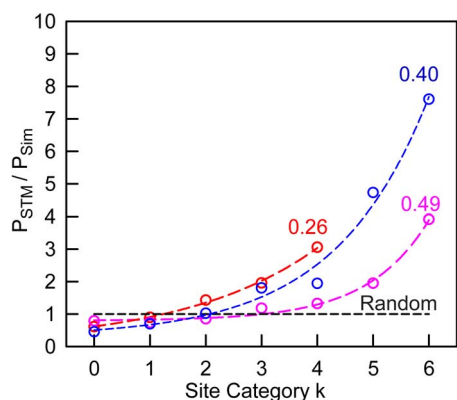
large (LH) range beyond the collision spot. The sizes of the clusters in Figs. 5(d)–5(f) are not large; the larger-than-expected pair correlation found in the small coverage of the extraction reaction sites is limited to the nearest neighboring sites $(s=1-4)$. These facts suggest that the reaction of Cl-extraction likely follows that of the HA process.

V. CONCLUSION

Distinguishing a detailed surface reaction mechanism has been an important but difficult issue. The $H_{(g)}$ $+Cl_{(ad)}$/Si(100) is an important prototypical system for the study of the ER, HA, and LH mechanisms. In our work, a combination of atomic resolved STM images, spectroscopic measurements of core level photoemission, and computer simulations provide a detailed picture of the atomic processes involved in this seemingly simple gas-surface reaction. The core level measurement and STM images observed the formation of $SiCl_2$ surface species, indicating that "some" additional reactions occur beside the removal of Cl upon impingement of H atoms. Analysis of the STM and simulated images shows that the Cl-extracted sites are correlated to the neighboring Cl-extracted sites. These experimental results cannot be explained by the pure Eley-Rideal process with unitary reaction probability. We recognize that other mechanisms, for example, an Eley-Rideal abstraction processes with a reaction probability which depends on the local surface coverage of Cl and maybe H, might possibly lead to our results. However, our findings and consideration lead us to believe that the HA process likely occurs during the atom-adatom collision. Further study is needed to better understand the nature of the gas-solid reactions.

FIG. 7. (Color online) The ratio of the population density obtained from a set of STM images P_{STM} to that from simulated images P_{Sim} vs site category k. The coverage of Cl-extracted sites in monolayer for each curve is labeled. The ratios obtained from several STM measurements and simulations vary slightly for each category, but their overall trends are the same.

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[28] There exists a possibility that the trajectory of an incoming H atom is slightly redirected by the Cl-extracted site to its close vicinity. However, our calculation based on the classical electrostatic force from surface dipoles suggests that the deflection is too small.