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Evaluating Mechanisms of Adsorbate Induced Roughening in Si(100) with Monte Carlo Simulations

D. A. Mirabella · C. M. Aldao

Abstract Halogen adsorption induces roughening of Si(100) producing pits and regrowth structures that depend on the type of adsorbed halogen and coverage. It is thought that this spontaneous roughening arises from steric repulsions between adsorbates. Recently, new interactions present in the Cl/Si(100) system have been suggested that can also contribute to altering the surface morphology. We used Monte Carlo simulations to determine the effects of the proposed interactions on the surface morphologies as a function of coverage.

Keywords Surface roughening · Monte Carlo simulations · Adsorbate–substrate interactions

1 Introduction

Regularly, in surface science and catalysis, substrates are considered rigid templates where adsorption and reactions take place. However, adsorbate induced restructuring and roughening have been observed in many crystal surfaces [1, 2]. The surface structure at the atomic level is crucial as it can directly affect many basic phenomena. Si(100), one of the most studied surfaces because of its relevance in semiconductor device fabrication, is an interesting candidate to test the effects of adsorbate–substrate interactions. Clean Si(100) reconstructs so that Si surface atoms pair to form dimers that align in rows. Since the energetics of

Si(100) is very well known it is suitable to perform computational simulations [3].

It has been observed that halogens roughen Si(100) without material removal at relatively low temperature [4]. Adsorbate–adsorbate steric repulsion was proposed to be the main interaction responsible for the spontaneous roughening of Si(100) [5]. In equilibrium, most Cl atoms on Si(100) are paired forming filled dimers that present significant steric repulsions. It is believed that these repulsions are the driving force for the observed surface morphology as roughening reduces the steric interaction contribution to the system total energy. However, roughening was observed at relatively low coverages for which adsorbates could distribute over the surface avoiding proximity and thus their interaction could be highly reduced.

More recently, other interactions were proposed. First, the adsorbate clustering due to substrate dimer anticorrelation interaction would offset the repulsion between adsorbates given rise to encounters between halogen filled dimers and then steric-induced roughening can be possible at low coverages [6]. Second, an adsorbate–substrate interaction related to the creation of preferential adsorption sites at steps has recently been reported [7]. This mechanism also leads to surface roughening by facilitating the creation of steps. Motivated by these interesting and controversial results and to gain insight into the mechanisms responsible for roughening, we undertook a systematic Monte Carlo modeling study of the substrate morphologies as a function of adsorbate coverage under the proposed interactions.

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2 Model Strategy

The Si(100) surface will be considered as built of Si dimers located at the sites of a regular simple cubic lattice with the

orientation of the dimer rows alternating between adjacent layers [8]. Since halogen molecules dissociate on Si(100) and they appear in pairs bonded to single dimers, a substrate particle can be considered a silicon dimer that is either bare or Cl covered. We could consider building the model using individual Si atoms but the price would have been very high in terms of computation. With this approach we could describe the dimer dissociation and formation at the atomic level. However, the intermediate species involved are very unstable and their density would be extremely low. In fact, experimentally they are not observed. On the other hand, the detailed energetics at the atomic level is not well known. Thus, this level of detail is unnecessary in our study since the basic features we aim to describe can be captured at the dimer scale.

Since silicon does not present voids or overhangs, we adopted the so-called solid-on-solid (SOS) model in which particles arrange in columns of different heights. Thus, the morphology of the substrate configuration is completely determined by a two dimensional array of integers equal to the heights of each column relative to the flat reference surface.

We explored two types of models, with first neighbor interactions and including second neighbor interactions between substrate particles. For the sake of simplicity, we will focus here on a model with only first neighbor interactions. The step-edge formation energy is given by $E_{x,y}/2$, where $E_{x,y}$ is the nearest-neighbor interaction in the x or y direction [9, 10]. Two types of steps are possible in Si(100); S_B that run perpendicular to dimer rows, and smooth S_A steps that run parallel to dimer rows [9]. Step formation energies are well known and then, consistently with reported values, we adopted $E_y = 0.24$ eV along rows and $E_x = 0.05$ eV across rows. As stated above, halogen molecules dissociate on Si(100) and then the surface is formed by bare or Cl covered dimers. Adsorption is dominated by the binding energy between adsorbates and substrate. However, the equilibrium surface structure does not directly depend on the strength of this energy but on the differences between configuration energies.

The standard Monte Carlo method of Metropolis was used to find the equilibrium configuration of the system [11]. The initial configuration is not relevant and we chose to assume that the initial surface is flat with adsorbates located at random. Two columns i and j were selected at random and a virtual transfer of a substrate particle from column i to column j was considered. If the system gained energy, the exchange was carried out. Otherwise, the exchange was performed with a probability $\exp(-\Delta E/kT)$ where ΔE is the loss of energy ($\Delta E > 0$). Next, an adsorbate and a bare site (without an adsorbate) were chosen at random; the adsorbate was moved to the new site according to the Metropolis rule. The system evolved with successive

jumps of adsorbates and substrate particles until it approached the equilibrium configuration. We ensured that the system reached equilibrium by monitoring the evolution of the surface roughening. Monte Carlo simulations were carried out in a square lattice of 100×100 sites and periodic boundary conditions were used to avoid edge effects.

3 Results and Discussions

Figure 1 shows a scheme to describe the type of interactions that will be studied in this work. Cubes represent substrate particles and spheres denote adsorbed particles. E_x and E_y indicate the substrate particle interactions. Case A depicts two neighboring adsorbates that interact. This adsorbate–adsorbate repulsion, AAR, accounts in the model for the steric effect in the Cl/Si(100) system. In case B, an adsorbate particle weakens substrate interactions (involved substrate particles are grey). In the Cl/Si(100) system, this interaction is related to the energy associated to anticorrelated tilted bare dimers. Finally, case C depicts a preferential step adsorption interaction (PSAI). In the Cl/Si(100) system, an interaction of this kind has been proposed to be present as adsorption at rebonded atoms along S_B step edges is energetically favorable. From the computational point of view, this preferential adsorption is equivalent to an attractive direct adsorbate–substrate lateral interaction [12].

The adsorbate steric-induced roughening has been tested by means of Monte Carlo simulations in a previous work [13] and could not reproduce the large features observed experimentally at low coverages under steady state. Figure 2 depicts the results of a MC simulation including steric repulsions showing the equilibrium configurations for a square lattice of 100×100 sites for Cl coverages of 0.1, 0.3, and 0.5 ML. The steric repulsion strengths used in our simulation were extracted from Ref. [6] (61 meV along
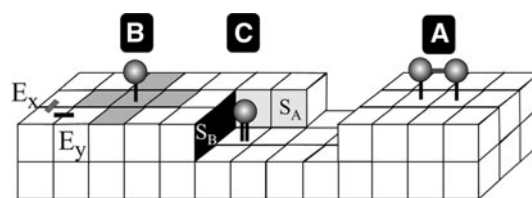
Fig. 1 Scheme that describes the interactions considered in modeling the evolution of a partially covered surface. *Cubes* represent substrate particles and *spheres* are adsorbates. E_x and E_y denote substrate particle interactions in the x and y directions, respectively. **A** depicts two neighboring adsorbates and their interaction. **B** shows an adsorbate particle that affects substrate interactions among *grey* substrate particles. **C** depicts an adsorbate interacting stronger with the substrate at a step
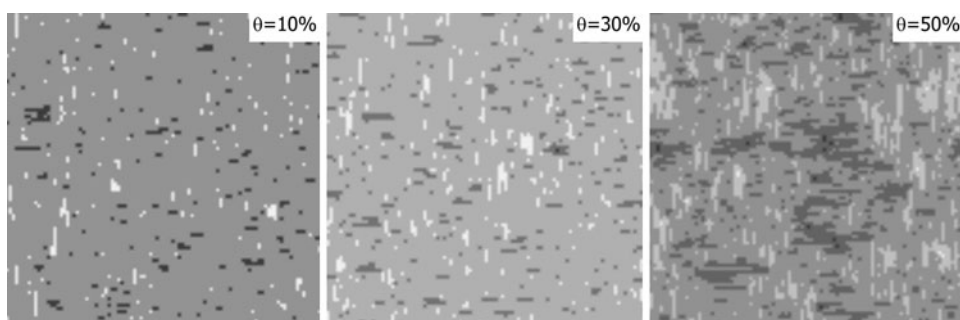
Fig. 2 Monte Carlo modeling outcome of a 100×100 lattice with coverages of 0.1, 0.3, and 0.5 ML after reaching equilibrium for the adsorbate–adsorbate repulsion (AAR) model. Adsorbate repulsions were 61 meV along y row direction and 26 meV across. Bright features are regrowth and dark features are pits. From this type of images, it was possible to determine the defect areas

the dimers row direction and 26 meV across). As expected, within this model not much roughening occurs in the low coverage regime because adsorbates have many available sites to avoid neighboring. Consistent with this argument, simulation outcomes only resembles the experimental morphology for $\theta = 0.5$ ML. Conversely, in contrast to the experimental observations for $\theta = 0.1$ and 0.3 ML that show significant roughening with features comprising several dimer rows [14], the width of simulated island and pit features are typically of only 1–2 dimer rows.

In equilibrium, most Cl atoms on Si(100) are paired forming filled dimers that, due to steric repulsions, would spread on the surface to reduce the total system energy. However, Cl adsorbed on Si(100) appears to be distributed uniformly on the surface indicating that there is no repulsion among adsorbates. After a detailed analysis of the experiments, Chen and Boland [15] showed that having two filled dimers next to each other in the same dimer row is energetically favorable by only 0.005 eV. Interestingly, similar calculations for hydrogen-filled dimers, which do not present a steric repulsion, show a clustering energy of 0.051 eV, in accord with other reported values. Indeed, in Ref. [16], using density functional theory, a hydrogen

clustering energy of 0.06 eV was determined and in Ref. [17], with STM results and Monte Carlo modeling, a value of 0.04 ± 0.2 eV was calculated. Thus, apparently, the clustering trend is not only a property of chlorine. In Refs. [15–17], the authors attribute this finding to the energy associated to anticorrelated tilted bare dimers. In Ref. [18] this possibility is discussed but the origin of clustering is eventually considered to be due to very subtle surface or near surface relaxation effects.

The two proposed interactions, adsorbate–adsorbate steric repulsion and clustering, have been considered to be responsible for the observed surface roughening [6]. It is argued that due to the clustering phenomenon, the probability of encounters between halogen filled dimers increases and then steric-induced roughening is possible at low coverages. We tested this idea by imposing to the adsorbates a uniform distribution on the surface but considering that there is a repulsion adsorbate–adsorbate that weakens the system and thus roughening is facilitated; this corresponds to the adsorbate–adsorbate repulsion with uniform distribution (AAR-UD) model. This implies that we adopted interdimer energies of 61 meV along the dimers row direction and 26 meV across. Figure 3 shows the resulting morphologies
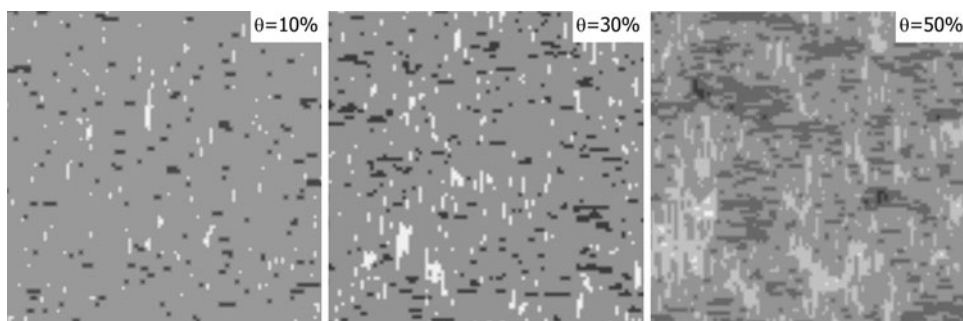
Fig. 3 Monte Carlo modeling outcome of a 100×100 lattice with coverages of 0.1, 0.3, and 0.5 ML after reaching equilibrium for the adsorbate–adsorbate repulsion with uniform distribution (AAR-UD) model. From an energetic point of view, adsorbate repulsions were 61 meV along row direction and 26 meV across but adsorbate particles are forced to be uniformly distributed on the surface. Interestingly, by comparing with Fig. 2, the uniform distribution of the adsorbates on the surface does not alter significantly the resulting morphologies
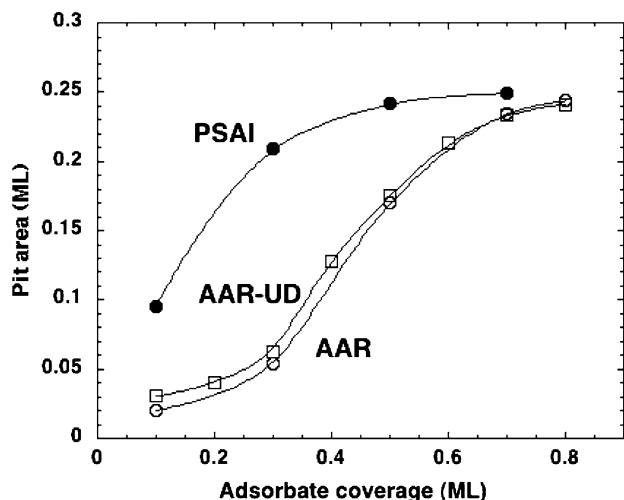
Fig. 4 Pit area for equilibrium surfaces as a function of the adsorbate coverage extracted from our Monte Carlo modeling. *Open circles* correspond to the adsorbate–adsorbate repulsion (AAR) model. *Open squares* correspond to the adsorbate–adsorbate repulsion with uniform distribution (AAR-UD) model. Differences between these two models are small. Filled circles correspond to the preferential step adsorption interaction (PSAI) model. The dependence of pit area on coverage is clearly different than those of previous models

of this model using Monte Carlo simulations. Surprisingly, the fact that now adsorbates are randomly distributed on the surface only slightly affects the resulting morphologies. Indeed, visual inspection of Figs. 2 and 3 indicates a negligible difference between the morphologies.

In order to quantify the surface roughening, the surface covered by pits as a function of coverage is plotted in Fig. 4 for some of the models we are presenting. In particular, note that the areas covered by pits for the AAR and the AAR-UD models only differ slightly. Far from being intuitive, it can be seen that imposing a uniform distribution of adsorbates on the surface has small effects on the resulting morphology. Since roughening directly depends on the adsorbate encounters, it is expected, as observed, that the surface damage increases very rapidly with the adsorbate coverage as the model shows. Although repulsion reduces the number of adsorbate neighbors a filled dimer has, the modeling helps us to determine in what

extent this occurs. Interestingly, for a coverage of 0.3 ML, the average number of first neighbors in the AAR model is only 30% smaller than in the AAR-UD model. This indicates that the used repulsion interactions do not prevent encounters between adsorbates as much as it could be expected and then roughening is only slightly affected.

In the case of being Cl the adsorbate, clustering interaction is completely compensated by the steric repulsion and then adsorbates are uniformly distributed on the surface. For hydrogen, the steric repulsion is negligible and then large patches of hydrogen form on a partially covered Si(100) surface. Clustering can be explained by considering that, along dimer rows, two adjacent doubly occupied dimers disturb three attractive interactions due to anticorrelated tilted bare dimers instead of four that are disturbed by two separated doubly occupied dimers. At first sight, this interpretation is very sound. However, this type of interaction should reduce the substrate particles interaction, an effect that we did not include in the AAR-UD model. This type of interaction is in fact similar to the repulsion between adsorbates particles and second neighbors of the substrate. This means that this interaction not only boosts roughening by helping repulsive adsorbates to be neighbors but, more important, it weakens the substrate.

Figure 5 shows the consequences of introducing in the Monte Carlo modeling the effect of reducing substrate particles interactions as the clustering mechanism suggests. The surface looks very rough from low coverages with small features covering completely the surface by $\theta = 0.3$ ML. By comparing these results with those corresponding to the AAR-UD model, we can infer that the main source of the roughening observed in Fig. 5 is the weakening of the substrate particle interactions. In order to verify that this is the case, in Fig. 6 we show the morphologies obtained without including repulsion. This would be the case of hydrogen, adsorbate that shows clustering without steric interactions. It is confirmed that the proposed mechanism for clustering would be a strong source of roughening due the reduction of the substrate particles interaction.

The above results lead us to reanalyze how clustering should be interpreted. Since adsorbates reduce the

Fig. 5 Monte Carlo modeling outcome of a 100×100 lattice with coverages of 0.1, 0.3, and 0.5 ML after reaching equilibrium for a model that includes adsorbate–adsorbate repulsion and the effect of reducing the substrate particle interactions due to clustering. Note that roughening is very strong from very low coverages
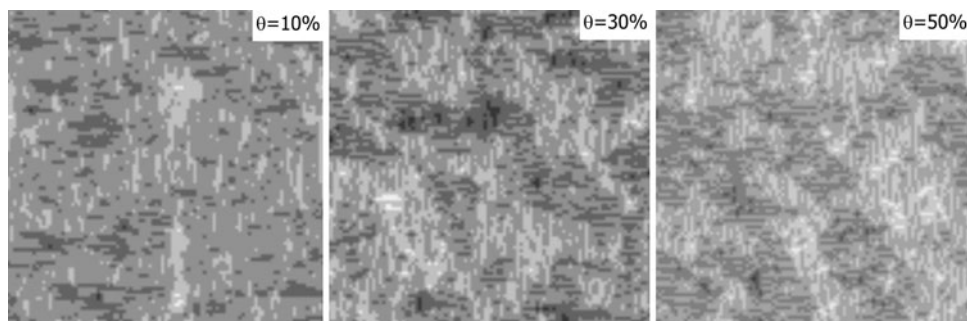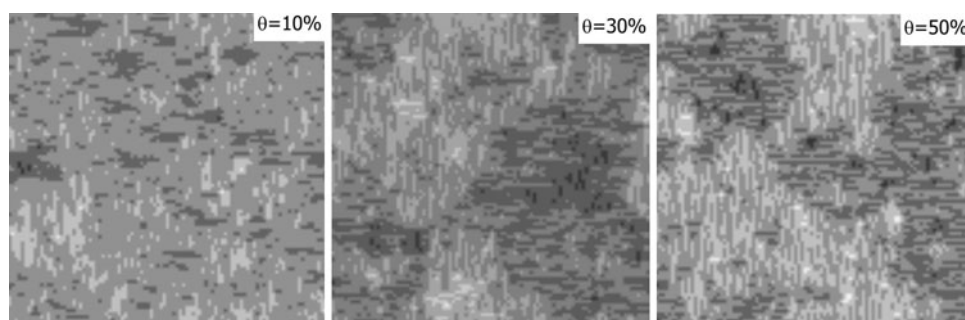
Fig. 6 Monte Carlo modeling outcome of a 100 × 100 lattice with coverages of 0.1, 0.3, and 0.5 ML after reaching equilibrium for a model that only includes the effect of reducing the substrate particle interactions due to clustering. Results indicate that the weakening of the substrate particle interactions is the main source of roughening in the model of Fig. 5

interactions among substrate dimers, clustering would favor the adsorption at all type of sites close to steps where substrate dimers have a lower number of neighbors. Experimentally this is not observed [7] and theoretically it was found that two Cl atoms adsorbed at a dimer close to a vacancy are just as energetically stable as they would be in an undamaged region of the surface [19]. One is then inclined to consider that adsorbate clustering does not affect the substrate energetics and that it is a consequence of an effective attractive interaction between adjacent doubly occupied dimer. Thus, the near random distribution of Cl on Si(100) indicates that clustering compensates the steric repulsion and the net Cl filled dimers interaction becomes almost negligible. Under this analysis, clustering and steric repulsion are interactions that cancel each other and then other mechanism should be responsible for surface roughening.

Recently, a different adsorbate–substrate interaction in the Cl/Si(100) system has been reported that can be responsible for stabilizing steps and then for surface roughening [7]. It was reported that Cl tends to adsorb at rebonded S_B step edged sites and the energy difference respect to sites at the terrace was calculated to be ~ 0.14 eV. This type of interaction corresponds to case C shown in Fig. 1, which makes energetically favorable the adsorption at sites close to steps on the lower terrace. By including this type of interaction, S_B step formation is facilitated. In Fig. 7 we show the consequences on surface

morphology when adsorption along dimer rows is 0.14 eV more favorable than at terraces. Simulations outcomes are more consistent with the experimental morphology reported in Ref. [14] showing large pits and regrowth islands at low coverages.

Roughening due to adsorbate–adsorbate repulsion is expected to be highly reduced for low coverages (AAR model). For a random distribution of adsorbates (AAR-UD model), the probability of encounters, which trigger the roughening interaction, goes as θ^2. Indeed, the surface covered by pits as a function of coverage in Fig. 4 shows this behavior. Conversely, in the PSAI model a lower coverage implies a lower disruption but any adsorbate particle can interact with steps at any coverage. Consistently with this argument, the surface covered by pits for this type of interaction has a very different dependence with coverage than that of the AAR or AAR-UD models, as observed in Fig. 4. The PSAI model presents a similar trend of the surface covered by pits to that found in experiments [13].

4 Conclusions

Monte Carlo simulations were used to explore the consequences of proposed halogen interactions adsorbed on Si(100) that promote surface roughening. The equilibrium surface morphology depends on the type of incorporated

Fig. 7 Monte Carlo modeling outcome of a 100 × 100 lattice with coverages of 0.1, 0.3, and 0.5ML after reaching equilibrium for the preferential step adsorption interaction (PSAI) model. Note that roughening leads to the formation of large and wide pits and islands as observed in experiments
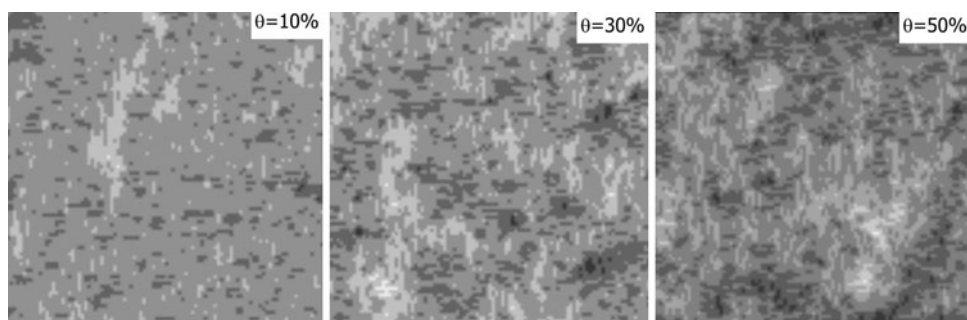
adsorbate–substrate and/or adsorbate–adsorbate interactions, on their strength, and on the adsorbate coverage. We studied the effects of adsorbate–adsorbate repulsion, adsorbate clustering, and direct adsorbate–substrate step interaction. We found that adsorbate–adsorbate repulsion, while it can roughens the substrate, does not reproduce the observed surface patterns. Adsorbate clustering leads to an unexpected strong roughening not compatible with experiments. Finally, simulations indicate that surface destabilization of the Cl/Si(100) system due to preferential adsorption sites at S_B steps shows the right trends in the resulting surface morphologies. This type of interaction naturally leads to pits and islands for low Cl coverages as observed in experiments.

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