

Surface roughening due to adsorbates

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Abstract

With a solid-on-solid model, we show how adsorbates can induce surface roughening. Roughened surfaces exhibit pits and regrowth structures that have characteristic patterns that depend directly on the adsorbate coverage and on the strength and type of involved interactions. Monte Carlo simulations were used to explore the consequences of adsorbate–adsorbate repulsion and two types of adsorbate–substrate interactions that lead to roughening.

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1. Introduction

Surface roughening during catalytic reactions is a well known phenomenon [1] but, in general, substrates are considered stable, as a static framework where adsorption and reactions take place. Due to the development of scanning tunneling microscopy, recent studies focus on the surface structures and their modifications at the atomic level (see for example [2]). However, the understanding of surface roughening induced by adsorption is a not a well-studied subject.

Recently, the structural changes at the atomic level that accompany spontaneous halogen etching of Si(1 0 0) have been subject of special interest [3–5]. These studies have shown that adsorbates like Cl can also roughen the surface without material removal at relatively low temperature [6,7]. Although adsorbate–adsorbate steric repulsion seems to be the main interaction responsible for roughening, Monte Carlo results indicate that the exact morphologies and coverage dependencies cannot be reproduced with a simple model if only adsorbate–adsorbate interactions are included [8]. Motivated by these findings and to gain insight into the mechanisms responsible for roughening, we undertook a systematic study of the substrate morphologies as a function of adsorbate coverage and three types of interactions that can roughen a surface.

Zhdanov and Kasemo [9] carried out similar studies on the decrease of the roughening temperature due to adsorption. Our work focused on the resulting surface structures due to different adsorbate interactions.

2. Model strategy

We adopted the so-called *solid-on-solid* (SOS) model in which particles arrange in columns of different heights such that overhangs and internal voids are not allowed. The morphology of the clean 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. Thus, the excess internal energy relative to a flat surface is related to the number of broken bonds.

We kept the model as simple as possible by adopting a Kosel crystal with first neighbor interactions and assuming that adsorbates can be located on top sites that can have at most only one adsorbate particle. The main interaction in adsorption is given by the binding energy between adsorbates and substrate. However, the equilibrium surface structure does not directly depend on the strength of the adsorbate binding energy but on the differences between configuration energies.

The first kind of interaction that we analyzed is the adsorbate–adsorbate lateral interaction. This kind of in-

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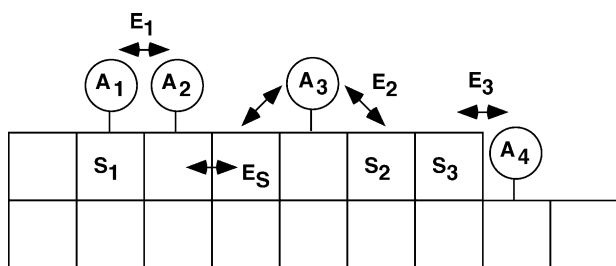


Fig. 1. One-dimensional schematic that describes three type of interactions due to adsorbates. Squares represent substrate particles and circles represent adsorbates. Arrows denote the interactions considered in this work. E_S represents the substrate particle interaction. E_1 represents a repulsion interaction between adsorbate particles. E_2 represents an indirect next-nearest-neighbor adsorbate–substrate interaction that can also be interpreted as a repulsion interaction between adsorbate particles and second neighbors of the substrate. E_3 represents a direct nearest-neighbor adsorbate–substrate lateral interaction between adsorbates and substrate particles. Note that movement of a substrate particle modifies not only the substrate energy but that in which the adsorbate particles are involved.

teraction, for example, has been interpreted in the halogen/Si(100) system as an steric repulsion [7]. Following Kasemo and Zhdanov [9], we also analyzed the effects of two types of interactions that take into account the influence of the local arrangement of substrate atoms on the binding energy. First, an adsorbate particle can weaken substrate interactions. This is called the indirect next-nearest-neighbor adsorbate–substrate interaction (innn-asi) that can be more easily seen as a repulsion interaction between adsorbate particles and second neighbors of the substrate. Second, we will analyze the effects of direct nearest-neighbor adsorbate–substrate lateral interaction (dnn-asli) between adsorbates and substrate particles.

We used the standard Monte Carlo method of Metropolis to find the equilibrium configuration of the system. The initial configuration is not relevant and we chose to assume that the initial surface is flat with adsorbates located at random. As dictated in the Metropolis method, two configurations need to be compared. Thus, 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

was now a loss of energy ($\Delta E > 0$). Then, an adsorbate and a bare site (without an adsorbate) were chosen at random. Again, the adsorbate was moved to the new site according to the Metropolis rule. Through successive jumps of adsorbates and substrate particles the system evolved until it approached the equilibrium configuration. Monte Carlo simulations were carried out in a square lattice of 100×100 sites and periodic boundary conditions were used to avoid edge effects.

Fig. 1 shows a one-dimensional scheme to describe the type of interactions taken into account in this work. Squares represent substrate particles and circles denote adsorbed particles. Note that moving a substrate particle can alter not only the interactions at the substrate but also the interactions between adsorbates. For example, if the substrate particle S_1 is removed from its present place, the repulsive interaction between the adsorbed particles A_1 and A_2 will disappear. Similarly, moving substrate particle S_2 reduces the interaction between A_3 and the substrate, and moving S_3 eliminates the lateral interaction between A_4 and the substrate. This type of considerations must be taken into account in calculating the energy of the initial and final configuration to apply the Metropolis rule.

3. Results and discussion

We explored a variety of substrate and adsorbate interaction values but we are particularly interested here in studying how a flat substrate can be affected by adsorbates. Our first goal is to choose an interaction between substrate particles leading to a surface with very few defects. In Fig. 2 we show snapshots of the equilibrium configurations corresponding to three values of the interaction energy between substrate particles, E_S . As expected, increasing E_S lowers the substrate roughness. Surface roughness can be defined as

$$\text{roughness} = \frac{\sum_i (h_i - \bar{h})^2}{\text{area}} \quad (1)$$

The number of defects is quite low for $E_S = 3kT$. Indeed, the structure of the clean surface derived from Monte Carlo modeling includes defects that cover only $\sim 0.3\%$ of the surface. This interaction energy leads to step energies similar to

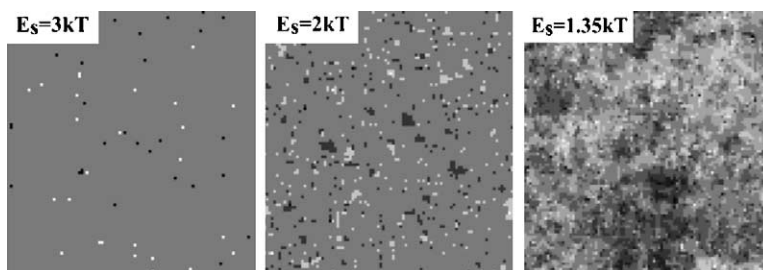


Fig. 2. Monte Carlo modeling outcome of a clean 100×100 lattice after reaching equilibrium where bright features are regrowth and dark features are pits. From this type of image it was possible to deduce the defect areas. Note that the surface looks very rough for a substrate interaction energy of $1.35kT$, with multilayer pitting but without the presence of large features.

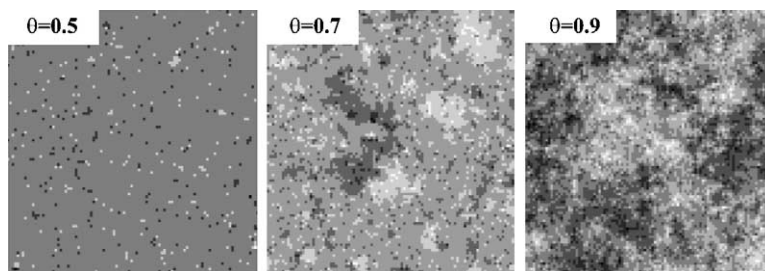


Fig. 3. Monte Carlo modeling outcome of a 100×100 lattice as a function of adsorbate coverage after reaching equilibrium including an adsorbate–adsorbate repulsion $E_1 = 0.5E_S$. Not much surface damage is observed for coverages $\theta < 0.5$ ML. Interestingly, large islands and pits appear at some intermediate coverages.

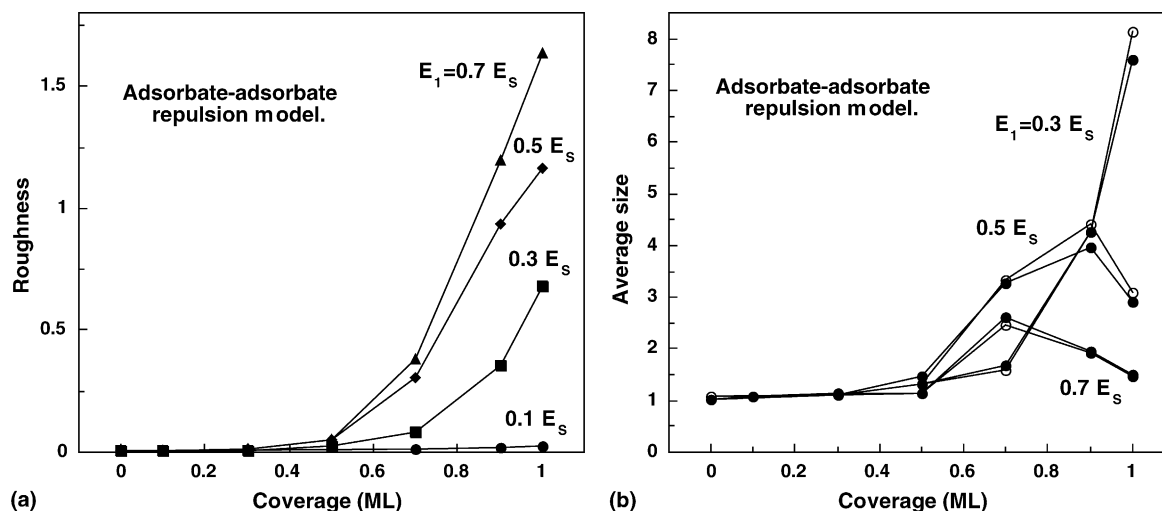


Fig. 4. (a) Roughness as defined in Eq. (1) for the adsorbate–adsorbate repulsion model. Significant surface modification is observed for coverages above 0.5 ML and interaction energies $E_1 \geq 0.3E_S$. (b) Average size of pits and islands for the adsorbate–adsorbate repulsion model as a function of coverage and interaction strength. Open circles denote pits and filled circles islands. Note that pits and islands present the same behavior.

those found in experiments and will be kept constant throughout this work [10]. Analysis of the resulting surface patterns shows that the number and distributions of pits and islands are similar and that large features do not form for any value of E_S .

We will next present results corresponding to a substrate in which adsorbate–adsorbate lateral interactions are incorporated. In Fig. 3 we show the resulting equilibrium patterns corresponding to a repulsion energy $E_1 = 0.5E_S$. For coverages $\theta < 0.5$, the adsorbates do not seriously affect the surface morphology. This is expected because the adsorption

geometry can minimize the adsorbate interactions by forming $c(4 \times 2)$ or $p(4 \times 4)$ patterns. However, local adsorbate density fluctuations can cause some roughening even at low coverages if the repulsive interactions are not strong enough to prevent adsorption on neighboring sites.

Fig. 4a shows the surface roughness due to adsorbate–adsorbate lateral interactions. As expected, the roughness increases with adsorbate coverage and repulsion interaction strength. The roughness shows a rapid increment above 0.5 ML as repulsion between adsorbates cannot be avoided. Fig. 4b shows the average size of islands

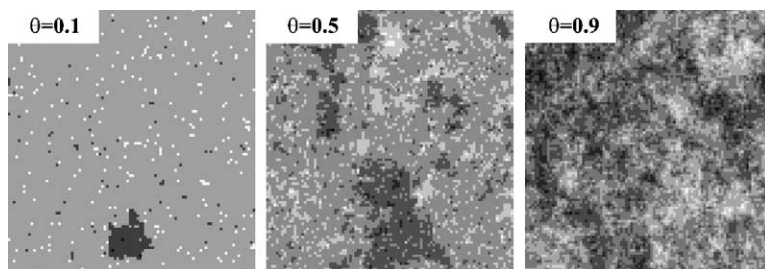


Fig. 5. Monte Carlo modeling outcome of a 100×100 lattice as a function of adsorbate coverage after reaching equilibrium including indirect next-nearest-neighbor adsorbate–substrate interactions with $E_2 = 0.4E_S$. Significant damage is observed from low coverages and big pits appear for some intermediate coverages.

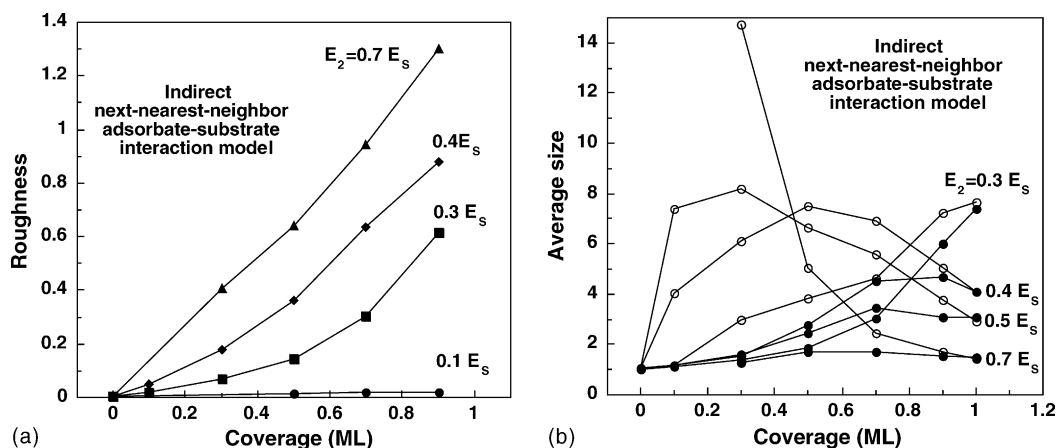


Fig. 6. (a) Roughness as defined in Eq. (1) for the indirect next-nearest-neighbor adsorbate–substrate interaction model. Surface roughness is a smooth function of coverage and interaction strength. (b) Average size of pits and islands for the indirect next-nearest-neighbor adsorbate–substrate interaction model as a function of coverage and interaction strength. Open circles denote pits and filled circles islands. Note that pits and islands do not present the same behavior.

and pits formed as a function of adsorbate coverage and repulsion interaction strength. For an adsorbate coverage of 0.3 ML, features increase monotonically with coverage up to an average size of about eight sites. For stronger repulsion interactions, the feature size increases with coverage up to a point where a higher coverage makes features smaller. Appar-

ently, for a strong enough repulsion interaction, adsorbates do not permit the existence of large flat regions as steps form to avoid neighboring adsorbate particles. The average size of pits and islands are the same since this type of interaction does not differentiate a step up from a step down and islands and pits reduce in the same amount neighboring adsorbates.

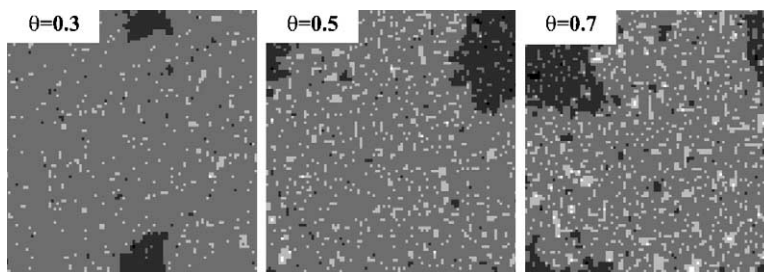


Fig. 7. Monte Carlo modeling outcome of a 100×100 lattice as a function of adsorbate coverage after reaching equilibrium including direct nearest-neighbor adsorbate–substrate lateral interaction with $E_3 = 0.5 E_s$. There is a clear tendency for the formation of big pits for high adsorbate coverages.

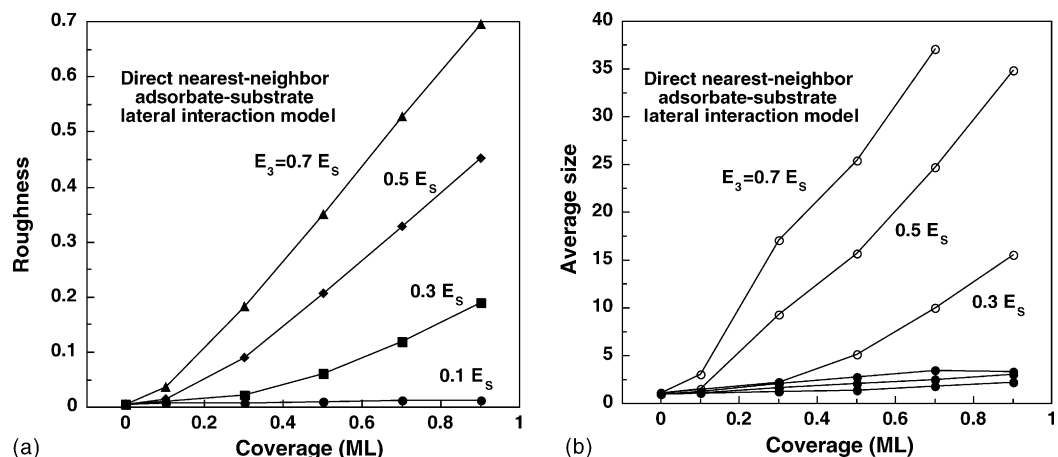


Fig. 8. (a) Roughness as defined in Eq. (1) for the direct nearest-neighbor adsorbate–substrate lateral interaction model. Surface roughness smoothly increases with coverage and interaction strength. (b) Average size of pits and islands for the direct nearest-neighbor adsorbate–substrate lateral interaction model as a function of coverage and interaction strength. Open circles denote pits and filled circles islands. Note that the average size of pits is a monotonous function of the coverage and that islands are small in all the studied range.

Next, we present the effects of indirect next-nearest-neighbor adsorbate–substrate interactions. Fig. 5 shows the equilibrium patterns for a second neighbor repulsion $E_2 = 0.4E_S$. Adsorbates affect the surface morphology from low coverages as individual adsorbates induce steps to lower the number of neighbors of the underlying substrate particles. Then, the surface could reduce its total energy by coalescing the formed features.

In Fig. 6a we show the surface roughness due to innn-asi as a function of adsorbate coverage with E_2 as a parameter. The roughness reflects the presence of the adsorbates from low coverages, presenting a smooth increase with coverage and interaction strength. Fig. 6b shows the average size of islands and pits formed as a function of adsorbate coverage and repulsion interaction strength E_2 . Results of the simulations present a rich behavior. To start, pits are systematically larger than islands. The substrate can reduce the system energy by forming large features, a tendency that is reflected in the formation of big pits as long as the repulsion strength and coverage are not too strong. Conversely, small islands are energetically favorable due to the type of involved substrate–adsorbate interaction. For example, an adsorbate particle on a single particle island can avoid four repulsion terms. This is not the case for a single site pit for which four adsorbates are needed to gain the same energy. Eventually, for a fully covered surface this distinction disappears and the resulting sizes of pits and islands become equal.

Finally, we present the effects of lateral interactions between adsorbate and substrate particles. We first considered that an adsorbate particle can interact with only one substrate particle. Fig. 7 shows the surface morphology corresponding to a lateral energy $E_3 = 0.5E_S$ for three coverages. The surface roughness increases with coverage and interaction strength as for the model with indirect next-nearest-neighbor adsorbate–substrate interactions (see Fig. 8a). Large pits form at low coverages and, at odds with the previous model, pits always increase with the coverage (see Fig. 8b). This is a consequence of the different characteristics of the studied interactions. In the innn-asi model, adsorbates prefer to be on top of small islands in order to reduce the number of substrate second neighbors. In the dnn-asli model, adsorbed particles interact attractively with only one step. Thus, in this model, an adsorbate particle with only one first neighbor of the substrate reduces the system energy as much as possible and pit splitting is not energetically favorable within the explored values of E_3 . Interestingly, in a model in which the adsorbate

particles interact with all the substrate first neighbors, the resulting surface morphology shows the opposite trend, i.e., there is a tendency to form small pits and thus the attractive interaction is maximized.

4. Conclusions

Monte Carlo simulations were used to explore the consequences of three possible interactions that lead to surface roughening. The modeling results indicate that the exact morphologies and coverage dependencies are not obvious. Resulting surface morphology due to adsorbates can be very different from simply reducing the strength of the substrate interaction or, equivalently, increasing the temperature. The specific equilibrium surface morphology depends on the type of adsorbate–substrate and/or adsorbate–adsorbate interactions included, on their strength, and on the adsorbate coverage.

Acknowledgments

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