A Lattice Model for Thermal Decoration and Step Bunching in Vicinal Surface with Sub-Monolayer Adsorbates

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We present a lattice model to study the “decoration” with the adsorbates on the stepped surface together with the step bunching induced by adsorbates. The model is the modified restricted solid-on-solid model coupled with Ising system (mRSOS-I model), where the energy reduction of the lateral bonds between the adsorbates on the different height of the surfaces is taken into consideration. We show, by Monte Carlo method, that the reduction factor \( \zeta \) is one of the key parameter for the decoration on the stepped surface in addition to another key parameter of the interplay factor \( \alpha \), which we previously introduced in the original RSOS-I model. The deposited islands appear from the down side, the upper side, or the both sides of the steps depending on the values of \( \zeta \) and \( \alpha \).

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I. INTRODUCTION

The interplay between surface steps and adsorbates is interesting itself as the surface science, and is important to fabricate nano- or micro-scale objects on the surface by use of the self-organization technique. In the adsorption process, the deposited islands appear from the down side, upper side, or both sides of respective steps depending on the combination of the atomic species of adsorbates and the substrate, and this phenomenon is called “decoration” [1]. Several kinetic processes [1–3] have been presented for such decoration phenomena as the non-equilibrium process.

In this paper, we present a lattice model which shows the decoration on the stepped surface, and show that the decorations on the down side, upper side, or both sides of the steps are controlled by two key parameters. The lattice model is the modified restricted solid-on-solid model coupled with Ising system (mRSOS-I model), whose lateral coupling constants between adsorbates are reduced at the step ledges. We show, by Monte Carlo method, that the reduction factor \( \zeta \) is one of the key parameter for the decoration on the stepped surface. We also show that the interplay factor \( \alpha \), which we previously introduced in the original RSOS-I model [4–6], is another key parameter for the decoration phenomena.

II. THE MODEL

A. RSOS-I model

In the previous paper [4–6], we have presented the RSOS-I model to study the vicinal surface with sub-monolayer adsorbates (Fig. 1). The Hamiltonian of the RSOS-I model is written as follows,

\[
H_{RSOS-I} = H_{RSOS} + H_{Ising} + H_{int}.
\]  

FIG. 1: RSOS-I model. (a) Perspective view of vicinal surface. Filled circles: adsorbates. (b) Top view of the model.
Here, $\mathcal{H}_{\text{RSOS}}$, which is the Hamiltonian of the restricted solid-on-solid (RSOS) model [7], is used to describe surface undulation (Fig. 1(a)), and is written as follows:

$$
\mathcal{H}_{\text{RSOS}} = \sum_{m,n} [\epsilon h(m+1,n) - h(m,n)] + \epsilon [h(m,n+1) - h(m,n)],
$$

where $b(n,m)$ is the surface height at the site of $(n,m)$, and $\epsilon$ is the microscopic ledge energy. The summation with respect to $(m,n)$ is taken all over the sites on the square lattice. The RSOS condition, where the surface height difference between nearest-neighbor $(mn)$ sites is restricted to $\{0, \pm 1\}$, is required implicitly.

$\mathcal{H}_{\text{Ising}}$, which is the Hamiltonian of the two-dimensional (2D) square Ising model equivalent to the 2D square lattice gas system, is used to describe sub-monolayer adsorbates system, and is written as follows:

$$
\mathcal{H}_{\text{Ising}} = -J \sum_{m,n} [\sigma_x(m,n)\sigma_y(m,n)
+\sigma_x(m,n)\sigma_y(m,n-1)\sigma_y(m,n-1)]
+H \sum_{m,n} [\sigma_x(m,n) + \sigma_y(m,n)],
$$

where $J$ is the nn coupling constant between Ising spins, and $H$ is the uniform external field. The adsorption sites are assumed to be the “bridge site” (Fig. 1(b)), and then the total number of adsorption sites is twice of the lattice sites of the RSOS model. The basic lattice vectors of the Ising square lattice rotate by 45 degrees relative to the ones of the RSOS model.

The physical meaning of $J$ and $H$ is seen by substituting the lattice gas variables $c(m,n) = (\sigma(m,n) + 1)/2$ into the Ising Hamiltonian Eq. (3). After the substitution, we obtain $\phi = 4J$, and $\mu = 2H - 8J = k_B T \ln P/P_0$ [4–6], where $\phi$ is the bond energy between adsorbates, $\mu$ is the relative chemical potential of adsorbates, $k_B$ is the Boltzmann constant, $T$ is the temperature, $P$ is the vapor pressure of adsorbates in the ambient phase, and $P_0$ is the vapor pressure so that $\mu = 0$.

$\mathcal{H}_{\text{int}}$ [4–6] is the Hamiltonian to describe the interplay between the surface steps and adsorbates, and is written as follows:

$$
\mathcal{H}_{\text{int}} = -\alpha \sum_{m,n} [\sigma_y(m,n)\sigma_y(m+1,n) - h(m+1,n) - h(m,n)]
$$

where $\alpha$, the interplay factor, is the only parameter we had introduced to describe the microscopic interaction between the adsorbate and the surface ledge. The microscopic ledge energy $\epsilon$ changes to $\epsilon(1 - \alpha \sigma)$, depending on the presence ($\sigma = 1$) and the absence ($\sigma = -1$) of the adsorbates.
B. Modification for the RSOS-I model

Let us introduce another parameter $\zeta$ as the “reduction factor” to describe more detailed microscopic interplay between the surface ledge and adsorbate.

The reduction factor is introduced in the following way. As is shown in the Fig. 2(a), the adsorbate on the ledge has two ways for its vertical location, which are shown in Figs. 2(b) and (c), respectively. Intuitively, it is plausible that the energy of the bond between the adsorbates on the different height of the surface (dotted line in Figs. 2(b) and (c)) will become smaller than the energy of the bond between the adsorbates on the surface with the same height (full line in Figs. 2(b) and (c)), since the distance between the adsorbates with the different height is larger than the one with the same height. We, therefore, describes the reduction of the bond energy as the reduction factor $\zeta$, and which is assumed to be 0.2, hereafter.

Then, only the Ising part of the RSOS-I model Hamiltonian is modified as follows,

$$
H'_{\text{Ising}} = -\sum_{m,n} [J_3(h)\sigma_x(m,n)\sigma_y(m,n) + J_4(h)\sigma_x(m,n)\sigma_y(m-1,n) + J_4(h)\sigma_x(m,n-1)\sigma_y(m,n) + J_2(h)\sigma_x(m,n-1)\sigma_y(m-1,n)] - H \sum_{m,n} [\sigma_x(m,n) + \sigma_y(m,n)],
$$

where $J_i(h)$ $(i = 1$ to $4)$ takes the value of $J$ or $\zeta J$ depending on the surface height configuration. We show the bond configuration explicitly in Fig. 3. When the adsorbate on the ledge sticks on the upper side of the ledge, the side view of the bond configuration is given by the Fig. 2(b), and the top view of the configurations is shown by the figures in the right column of the Fig. 3. While the adsorbate sticks on the down side of the ledge, the side view of the configuration is given by the Fig. 2(c), and the top view of the configurations is shown by the figures in the middle column of the Fig. 3. We designate the former case as the upper side model, and the latter case as the down side model. Then, the Hamiltonian of the modified RSOS-I (mRSOS-I) model becomes as follows:

$$
H_{\text{mRSOS-I}} = H_{\text{RSOS}} + H'_{\text{Ising}} + H_{\text{int}}.
$$

Due to the reduction factor $\zeta$, the boundary line tension around the deposited islands is partially released on the step ledge in the vicinal surface. The islands of adsorbates, therefore, stay in the neighborhood of step ledges. In the 1×1-to-7×7 phase transition on Si(111), the 7×7 domain can be considered as the adsorbate island. This scenario is the same as the one discussed by Hibino et al. [8] to phenomenologically explain the 7×7 domain formation in the 1×1 structure. The mRSOS-I model could give microscopic foundation to the scenario.

III. MONTE CARLO SIMULATION

By use of the Monte Carlo calculation on the mRSOS-I model, we demonstrate that the model shows the deco-
less than the $H_c$ above which the spinodal decomposition occurs.

We show the snapshots of the down side model obtained by the Monte Carlo method in Fig. 4. The reduction factor $\zeta$ plays the role of the key parameter for the decoration phenomena. Due to $\zeta < 1$, the boundary line tension around the deposited islands is partially released on the step ledge in the vicinal surface. The islands, therefore, tend to stay in the neighborhood of step ledges on the substrate surface.

Another key parameter is the interplay factor $\alpha$. In the case of $\alpha > 0$ ($\alpha < 0$), the islands appear from the down (upper) side of the step ledge, and they stay near the step on the terrace with the down (upper) side of the step on the surface. While for $\alpha = 0$, the islands appear from the both sides of the step ledge, and they spread on the terraces with the both sides of the step.

Here, we show the snap shots obtained by the Monte Carlo method for the upper side model in Fig. 5. As is seen from the figure, the islands appear in the similar way as the case of the down side model for $\alpha = 0$. In the case of $\alpha > 0$ ($\alpha < 0$), the islands appear and stay on the terrace on the opposite side of the terrace in the down side model with respect to the step line. It should be noted that, in the both models, the islands appear asymmetrically with respect to the step line when $\alpha \neq 0$.

In order to see the difference between the original RSOS-I model and the modified RSOS-I model, we show the snap shots obtained by the Monte Carlo method for the original RSOS-I model in Fig. 6. In the original RSOS-I model, islands appear from the step ledge for $\alpha > 0$, and from the terrace for $\alpha < 0$. For the case of $\alpha = 0$, islands appear irrespective of the surface configuration. Even for $\alpha > 0$, the islands appear symmetrically with respect to the step line. As described above, the asymmetry on the island appearance with respect to the step line is induced by the reduction factor $\zeta$.

In order to see the surface configuration near equilibrium, we have made the long time Monte Carlo calculations. We show the snapshots of the vicinal surface in Fig. 7 for the down side model. In the case of $\alpha < 0$, steps self-assemble to form a faceted macro step. The thermal step bunching is caused by the interplay between the surface steps and adsorbates. The wide terrace is covered with adsorbates almost completely, while, the tilted surface formed by bunched steps is kept to be clean. Qualitatively, such long time behaviors are common among the
FIG. 7: Long time behavior of the vicinal surface with adsorbates ($\mu > 0$). Snap shots of the top view of the mRSOS-I model with the down side one ($H > 0$). Brightness: surface height (brighter $\rightarrow$ higher). Purple dots: adsorbates. Lattice size: $100 \times 60$. $H/\epsilon (\mu/(2\epsilon)) = 0.004$. $\zeta = 0.2$. $J/\epsilon (\phi/(4\epsilon)) = 0.35$. $k_B T/\epsilon = 0.3$. (a) Initial configuration. The coverage of adsorbates: 0.5. (b) $\alpha = 0.5$. 10000 MCS/site. (c) $\alpha = 0$. 50000 MCS/site. (d) $\alpha = -0.5$. 40000 MCS/site.

original RSOS-I model [4, 5] and mRSOS-I models with the upper and down side ones.

B. The case of $H < 0$

In the case of $H < 0$, adsorbates evaporate from the stepped surface. We show the snapshots of the early stage of evaporation of adsorbates obtained by the Monte Carlo method for the down side model in Fig. 8, and show the ones of the long time behavior of the vicinal surface with sub-monolayer adsorbates in Fig. 9. For $\alpha > 0$ ($\alpha < 0$), the void areas surrounded by adsorbates appear from the upper (down) side of the step. While for $\alpha = 0$, the void areas appear from the both sides of the step.

In the long time behavior near equilibrium, steps bunch in the case of $\alpha > 0$. The wide terrace is almost clean. On the other hand, the tilted surface formed by bunched steps is covered with adsorbates.

IV. SUMMARY

We have presented the modified restricted solid-on-solid model coupled with Ising system (mRSOS-I model) to study the decoration on the stepped surface with adsor-
FIG. 9: Long time behavior of the vicinal surface with adsorbates ($\mu < 0$). Snap shots of the top view of the mRSOS-I model with the down side one ($H < 0$). Brightness: surface height (brighter $\rightarrow$ higher). Purple dots: adsorbates. Lattice size: $100 \times 60$. $H/\epsilon (\mu/2\epsilon) = -0.004$. $\zeta = 0.2$. $J/\epsilon (\phi/(4\epsilon)) = 0.35$. $k_B T/\epsilon = 0.3$. (a) $\alpha = 0.5$. 500000 MCS/site. (b) $\alpha = 0.3$. 000000 MCS/site. (c) $\alpha = -0.5$. 100000 MCS/site.

In the mRSOS-I model, the modification of the lateral coupling constants between adsorbates on the different surface heights is taken into consideration as the reduction factor $\zeta$. Due to the modification, the boundary line tension around the deposited islands is partially released on the step ledge in the vicinal surface. The islands of adsorbates, therefore, stay in the neighborhood of step ledges. In the $1 \times 1$-to-$7 \times 7$ phase transition on Si(111), the $7 \times 7$ domain can be considered as the adsorbate island. This scenario is the same as the one discussed by Hibino et al. [8] to phenomenologically explain the $7 \times 7$ domain formation in the $1 \times 1$ structure. The mRSOS-I model could give microscopic foundation to the scenario.

Another key parameter $\alpha$, the interplay factor which was introduced in the original RSOS-I model [4–6], determines from which side of the step ledge the decoration appears.

By Monte Carlo method with the Metropolis algorithm of the importance sampling, we show the decorations on the stepped surface of the mRSOS-I model of Fig. 2(c), together with the thermal step bunching induced by the adsorbates. Then we demonstrate that the decorations in the down side, the upper side, or the both sides of the steps are simulated by changing the parameters $\alpha$ and $\zeta$.

In the case of $H > 0$ ($\mu > 0$), the mean coverage of adsorbates becomes large (near 1). If $\alpha > 0$ ($\alpha < 0$), islands of adsorbates appear from the under (upper) side of the step. In the long time limit, steps self-assemble to bunch due to the adsorbates for the case of $\alpha < 0$.

While in the case of $H < 0$ ($\mu < 0$), the mean coverage of adsorbates becomes small (near 0). If $\alpha > 0$ ($\alpha < 0$), the void areas surrounded by adsorbates appear from the upper (under) side of the step. In the long time limit, steps bunch for the case of $\alpha > 0$.

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