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Coverage-dependent Collective Diffusion of Dense Pb Wetting Layer on Si(111)

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Abstract

The dynamics of dense Pb wetting layer on Si(111) surface is studied in the framework of a generalized Frenkel-Kontorova model. Instead of the typical diffusion by random hopping processes, a liquid-like collective motion of the Pb atoms within the dense wetting layer is revealed to give rise to ultrafast kinetics of the wetting layer even at low temperatures. A kinetic Monte Carlo simulation including this collective spreading mechanism of the dense wetting layer quantitatively reproduces the experimental observations.

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Surface diffusion plays a crucial role in a wealth of physical processes such as chemical reactions and catalysis, growth of crystals and thin films, and formation of nanostructures via self-assembly or cluster deposition. As such it has been a subject of extensive experimental and theoretical studies.[1–4] So far, mass transport at surfaces is generally believed to proceed either (i) by single adatom jumping from one surface site to another or (ii) by cooperative processes involving simultaneous motion of two or more atoms, with the latter mechanism especially relevant in homoepitaxial metallic systems. In heteroepitaxial growth, the deposited materials initially form a wetting layer on the substrate surface. Subsequent growth via adatom diffusion and nucleation then takes place on top of the wetting layer. Despite intensive investigations of atomic diffusion on various substrates, the particle dynamics within dense wetting layers and its role in surface mass transport remains largely unexplored.

Very recently, the mass transport in Pb wetting layer on Si(111) surface has been studied by monitoring the temporal evolution of nonequilibrium coverage profiles using low energy electron microscopy (LEEM).[5] The initial coverage step profile was found to propagate rapidly at constant velocity ($\Delta x/\Delta t$) with an unperturbed shape. This is very unusual because it contradicts the classical behavior characterized by profile broadening with $\Delta x/\sqrt{\Delta t}$ remaining constant during gradual equilibration. In addition, the equilibration time of the step profile exhibits a strong coverage dependence, and an exponential divergence below a critical coverage θ_c . These observations have revealed intriguing dynamics of the Pb wetting layer. However, the nature of the fast mass transport in the Pb wetting layer on Si(111) is still not well understood.[5, 6]

It has been proposed that the fast mass transport in the Pb wetting layer is facilitated by the thermally generated adatom diffusion on top of the wetting layer. A linear dependence of vacancy-adatom formation energy E_c with Pb coverage in a ratio of 0.55 eV/0.1 ML is assumed in order to account for the exponential divergence of the equilibration time observed in the LEEM experiment.[5] To check the validity of the proposed diffusion model, we first performed first-principles calculations to evaluate E_c for the Pb wetting layer of different coverages using the VASP code.[7, 8] The calculations reveal that E_c is either negative or small positive values (< 0.25 eV) for all the dense Pb wetting layers considered. This result is expected because of the incommensurate nature of the strongly compressed Pb overlayer on Si(111) at high coverages. This result does not support the assumption proposed in Ref.

5. Therefore, the conventional adatom diffusion mechanism cannot explain the divergent behavior of the equilibration time below θ_c .

In this Letter, we examine the intriguing dynamics of the Pb wetting layer on Si(111) by molecular dynamics (MD) simulations using a generalized Frenkel-Kontorova (FK) model. Our study demonstrates that the fast mass transport arises from a collective liquid-like motion of the Pb atoms within the dense wetting layer, rather than the typical uncorrelated random individual atom hopping. Results from a kinetic Monte Carlo (KMC) simulation including the collective spreading mechanism of the dense wetting layer are consistent with the experimental observations.

The choice of the generalized FK model[9, 10] was motivated by the fact that it is the simplest model which takes into account the main features of real surface adsorbate systems. The atoms in the overlayer are represented by a chain of atoms, which are assumed to be mobile in two directions, one along the surface (i.e., along the chain), and the other normal to the surface. The interaction between adatoms are described by a generalized Morse potential, and their interaction with the surface is represented by a substrate potential which is periodic along the chain and has the shape of a Morse potential in the normal direction. The coverage of atoms is characterized by a dimensionless parameter $\theta = N/M$, where N is the number of atoms and M is the number of minima of the substrate potential. The static energy of the chain is given by:

$$\begin{aligned}
 H = & \sum_{i=1}^N \left[\frac{1}{2} \varepsilon_s (1 - \cos(2\pi x_i/b)) e^{-\zeta' y_i} + \varepsilon_d (e^{-\zeta y_i} - 1)^2 \right] \\
 & + \sum_{i=1}^{N-1} \sum_{j>i}^N \varepsilon_a [e^{-2\alpha(r_{ij}-a)} - 2e^{-\alpha(r_{ij}-a)}]
 \end{aligned} \tag{1}$$

where the exponential factor in the first term on the right-hand side of Eq. (1) takes into account the decreasing influence of the surface corrugation as the atoms move away from the surface, ε_a is the dissociation energy of atoms in the chain, a is the equilibrium interatomic distance between the overlayer atoms, and ε_s and b are the amplitude and period of the substrate potential along the chain, respectively. The parameter ζ is related to the frequency of atom vibration in the normal direction, and ε_d the adsorption energy. For the Pb/Si(111) system, we have $b = 3.84\text{\AA}$, $a = 3.5\text{\AA}$, and $\varepsilon_s \sim 0.2$ eV, $\varepsilon_d \sim 3$ eV. The Morse potential parameters for Pb were developed by Girifalco and Weizer.[11]

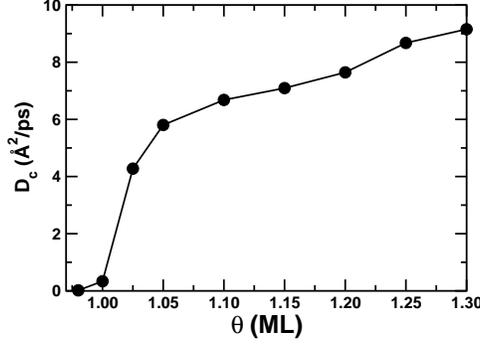


FIG. 1: Dependence of collective diffusivity on the coverage of the wetting layer derived from molecular dynamics simulations at 300 K.

Using the above potential molecular dynamics simulations based on Langevin equations are carried out to explore the dynamics of the system. Periodic boundary conditions are imposed with a fixed number of minima (M) of the substrate potential as well as a fixed number of N adatoms at each coverage. Using the atomic trajectories $\vec{R}_i(t)$ from the MD runs, the collective diffusion coefficient at each coverage, $D_c(\theta)$, can be deduced from the decay of spontaneous density fluctuations in the system. The fourier transform of the density-density correlation function gives the intermediate scattering function, $F(q, t)$, defined as

$$F(q, t) = \frac{1}{N} \left\langle \left(\sum_{j=1}^N e^{-i\vec{q} \cdot \vec{R}_j(t+t_0)} \right) \left(\sum_{l=1}^N e^{i\vec{q} \cdot \vec{R}_l(t_0)} \right) \right\rangle, \quad (2)$$

In the hydrodynamic limit $q \rightarrow 0$, $F(q, t)$ can be written as[12]

$$\frac{F(q, t)}{F(q, 0)} = \frac{\gamma - 1}{\gamma} e^{-D_c q^2 t} + \frac{1}{\gamma} e^{-\Gamma q^2 t} [\cos(c_s q t) + b(q) \sin(c_s q t)], \quad (3)$$

where c_s is the adiabatic velocity of sound, $\gamma = C_p/C_v$ is the ratio of the specific heats, Γ is the sound attenuation coefficient, and D_c is the collective diffusivity, $b = (q/c_s)\Gamma + (\gamma - 1)D_c$. All these parameters are q -dependent quantities (here the wave vectors q have to satisfy the condition $q = n \frac{2\pi}{L}$, n are integers, $L = 5000a_{Si(111)}$).

The calculated $F(q, t)$ is fitted to the expression of Eq. (3), using a standard least-square fit procedure. The functional form of Eq. (3) seems to fit well to our MD data when the coverage of the wetting layer is close to and higher than 1 ML. We calculate values of D_c for q between 0.23 and 0.49 \AA^{-1} and obtain the long range physical diffusion coefficient by extrapolating them to $q = 0$. Figure 1 shows the coverage dependence of the collective

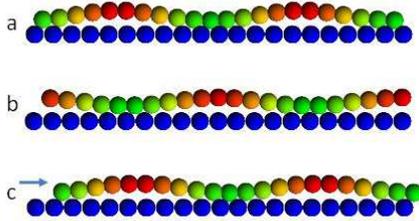


FIG. 2: Schematic representation of the motion of atomic chain within the generalized Frenkel-Kontorova model. From (a) to (c), the group of atoms collectively moves one lattice parameter to the right.

diffusion coefficient D_c of the overlayer atoms. It can be seen that atomic diffusion is negligible when the Pb coverage is below 1 ML. However, the diffusivity increases dramatically above 1 ML. The collective diffusion coefficient at higher coverages is comparable to that of bulk Pb liquid above the melting temperature.[13] In this sense, the dense Pb wetting layer can be considered a liquid-like film with ultrafast particle dynamics within it. Recent STM experiment also observed that Pb was transferred to the top of unstable islands, not via independent atom hops, but by a continuous spreading of the wetting layer.[14]

To identify the mechanism of this intriguing dynamical behavior, we examine the “movie” presentation of the atomic trajectories from the MD simulations and observe concerted atomic motion in the system. As exemplified in Fig. 2, the atomic motion of the generalized FK chain is similar to the motion of a caterpillar, forming a liquid-like particle wave when the coverage is larger than 1 ML. The transient assembly of atoms shown in Fig. 2 comes very close to what is usually called a soliton,[15–18] and the feature becomes more pronounced with increasing coverage. The formation of soliton is due to the lattice mismatch between the overlayer and the substrate, which gives two competing tendencies in the arrangement of Pb atoms on Si(111). On one hand, Pb atoms are drawn to the minima of substrate potential, on the other hand, they try to form a lattice with a period of a . Once the soliton is formed, it propagates with almost zero diffusion barrier[15–18] and introduce concentration variations in the system. The motion of solitons thus gives rise to a fast collective diffusion mode which dominates over hopping of individual atoms in the wetting layer and produces unexpected high mobility for mass transport in heteroepitaxial systems especially at low temperatures.

Using the coverage dependent diffusion coefficients shown in Fig. 1, we now show that a continuum diffusion equation below can reproduce the novel features for the dynamics of Pb wetting layer on Si(111) described earlier.

$$\frac{\partial\theta}{\partial t} = D_c(\theta) \left(\frac{1}{r} \frac{\partial\theta}{\partial r} + \frac{\partial^2\theta}{\partial r^2} \right) + \frac{\partial D_c(\theta)}{\partial\theta} \left(\frac{\partial\theta}{\partial r} \right)^2, \quad (4)$$

We have numerically integrated Eq.(4) using the finite-difference method. The temporal evolution of coverage profiles and front positions obtained by numerical solutions are shown in Fig. 3(a) and 3(b), respectively. It is interesting to see that the experimentally observed behavior of invariant profile shape and constant filling speed after a short initial time period are well reproduced using the $D_c(\theta)$ obtained from the generalized FK model. This dramatic deviation from classical behavior is caused by the large difference in the diffusion coefficients at the high and low coverage regions. One can expect that the profile shape will not remain so abrupt and the moving edge speed will not be constant when the ratio of diffusion coefficients outside and inside the hole is not large enough. To explore the situation where the profile broadening will be seen, we have performed calculations with a model $D_c(\theta)$ of the form $D_c(\theta) = \frac{D_1 - D_2}{1 + e^{-\frac{\theta - \theta_c}{w}}} + D_2$ (where D_1 and D_2 are the values of diffusion coefficients at low and high coverages, w is the transition coverage width from D_1 to D_2) as suggested in Ref. 6. Different values of the ratio D_2/D_1 have been considered. The transition from dispersionless diffusion to classical behavior occurs around a ratio of $3 \sim 4$ when $w=0.1$ and $D_1=0.05$.

As discussed above, at high coverages ($\theta \geq 1$ ML), strong interactions between the adatoms cause their motion to take on a collective (concerted) character described by solitons. In this case the activation energy E_a becomes the Peierls-Nabarro barrier E_{PN} , significantly lower than the individual activation energy,[9] leading to the observed fast wetting layer dynamics even at low temperatures. However, at low coverages ($\theta < 1$ ML), the mass transport mainly involves individual processes when an adatom directly jumps from one adsorption site to the next adsorption site. The diffusion coefficient in this case follows the Arrhenius law $D(T) = D_0 \exp(-E_a/k_B T)$. It is very reasonable to expect that such different diffusion mechanisms observed in 1D systems should also occur in 2D systems. MD simulations based on a 2D FK model for smaller size unit cells show that the collective diffusion increases sharply when the coverage is above 1 ML although the quantitative values of the diffusion constants obtained are not as accurate as the 1D simulations because of the limited cell size.

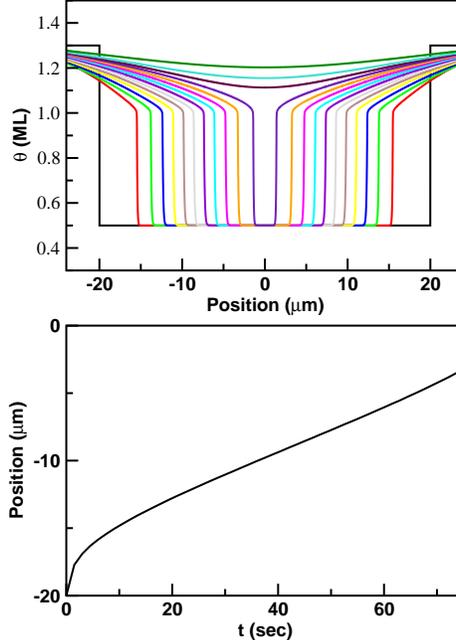


FIG. 3: Temporal evolution of coverage profiles and front positions obtained by numerically solving the diffusion equation for the initial wetting layer coverage of 1.3 ML.

It is computationally beneficial to incorporate the different diffusion mechanisms at high and low coverages into a semi-discrete KMC model to describe the mass transport behavior observed in recent LEEM experiment.[5] As shown in Fig. 4(a), our KMC model consists of three parts: (1) region A: the wetting layer outside the hole, which is treated as a continuum and assumed to have a constant coverage of θ_A because of the fast continuous spreading feature in region A and its large area relative to the hole; (2) region B: the hole represented by a discrete lattice of sites, which may be either occupied or vacant; and (3) region C: the hole region right next to the wetting layer, represented by a single site with occupation 0 or 1. The initial configuration inside the hole is randomly generated with a coverage of $\theta_B = 0.5$ ML. Three relevant diffusion processes are taken into account: (1) the step edge can propagate towards the middle of the hole ($A \Rightarrow C$) if site C is empty; (2) Pb atoms in the hole can diffuse back and forth ($B \Leftrightarrow C$) following usual KMC rules; and (3) Pb atoms in the hole next to the step edge can diffuse out of the hole ($C \Rightarrow A$) at a constant rate. The diffusion rate of each process can be expressed as $r_i = \nu_i \exp(-E_i/k_B T)$. Here ν_i is an attempt frequency (typically of 10^{12} s^{-1}) and E_i denotes the activation barrier. Given the coverage-dependent collective diffusion behavior from the MD simulations above, we assume that $E_{A \rightarrow C}$ linearly

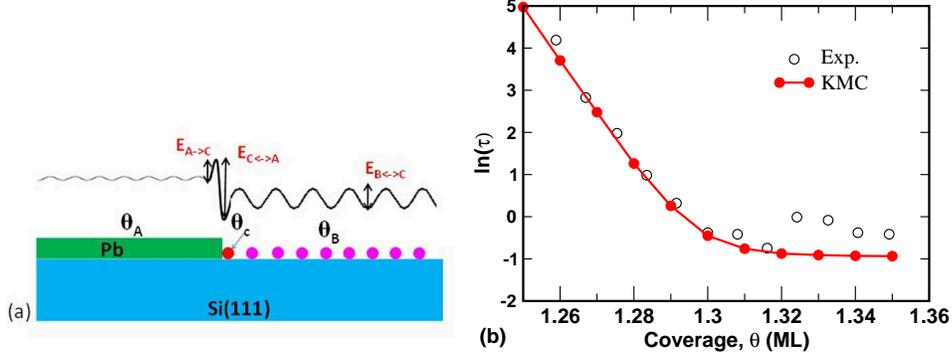


FIG. 4: (a) Schematic representation of the energy landscape in our semi-discrete KMC model. The coverage of the wetting layer is θ_A ; the coverage in the hole is θ_B ; and θ_C is the coverage in the boundary. $E_{A \rightarrow C} = -3.31\theta_A + 4.453$ eV, $E_{B \leftrightarrow C, B \leftrightarrow B} = 0.18$ eV, and the hopping barrier back to the wetting layer is $E_{C \rightarrow A} = 9.8$ eV. (b) The dependence of the equilibration time upon the wetting layer coverage at 341 K.

decreases with the coverage of the wetting layer, $E_{A \rightarrow C} = -3.31\theta_A + 4.453$ eV. $E_{C \rightarrow A}$ is set to be a large value of 9.8 eV since the probability to jump back to the wetting layer is little. The hopping barrier inside the hole is 0.18 eV. The choice of these effective barriers is reasonable as guided by existing experimental measurements and simulation predictions.[5, 14, 19, 20]

The profile evolution of the Pb wetting layer is determined as average over a series of KMC simulations (~ 100 times) in order to decrease statistical fluctuations. The resulting coverage dependence of equilibration time are compared with the experimental results in Fig. 4(b). It can be seen that the coverage dependence of equilibration time are well reproduced in the KMC simulation, i.e., the exponential divergence of equilibration time below the critical coverage θ_c (1.3 ML). When the wetting layer coverage is below θ_c , the step barrier $E_{A \rightarrow C}$ is larger than the diffusion barrier in the hole, implying that supply of Pb atoms from the wetting layer is the rate-limiting step for mass transport. As the wetting layer coverage increases, the step barrier linearly decreases and becomes smaller than the diffusion barrier in the hole at high coverages. The current from the wetting layer to the hole moves so fast that this process is no longer a rate-limiting step. The equilibration time is thus dominated by the transport in the hole and not sensitive to the wetting layer coverage when $\theta > \theta_c$.

In summary, the anomalous mass transport in Pb wetting layer on Si(111) surface observed in recent experiment has been addressed by MD simulations using a generalized FK

model and KMC simulations. Our MD simulation results show that the dense Pb wetting layer on Si(111) exhibits ultrafast liquid-like dynamics due to the formation of solitons. The temporal evolution of nonequilibrium coverage profiles observed in the experiment can be understood by a continuum diffusion model based on the coverage-dependent diffusion coefficients obtained from our MD simulations. The exponential divergence of equilibration time below the critical coverage is governed by the coverage-dependent activation barrier to flow into the hole, as suggested from our KMC simulations.

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