

Simulation of oxidized silicon stripe formation on Pd(111)

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We propose the model with two interaction constants (nearest neighbour pair repulsion of SiO complexes and their trio attraction in a line) which demonstrates stripe formation during silane decomposition on oxidized Pd(111) surface. The simplest (2×1) stripe phase is obtained by kinetic Monte Carlo simulation in absence

of longer-range attractive interactions which are usually necessary for stripe structure formation. Despite higher energy, this phase is shown to be very stable. Phase diagram for this model is obtained, and (2×1) phase stability is analyzed varying coverage and reaction rate parameters.

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1 Introduction Recently several papers [1–3] were published on room temperature decomposition of silane (SiH_4) on oxidized Pd and Pt(111) surfaces. Room temperature fits into a narrow temperature where silane already decomposes, but the temperature is insufficient for formation of various silicides. The most striking result of these experiments was the discovery of Si-O stripe structure. This result was confirmed by vibrational spectra measurements [2] and supported by density functional theory (DFT) calculations [3]. According to the DFT results, at low silicon coverage the SiO complex (Si atom with O atom in an “on-top” position) is initially formed. With increase of Si concentration such SiO complexes start to connect into correlated chains (stripes) with O shifted into a “bridge” position between two Si atoms. It should be noted that formation of stripes is usually possible in a systems with competing short- and long-range forces, e.g. binary mixtures, Langmuir films, or ferromagnetic systems with competing ferromagnetic exchange and antiferromagnetic dipole interactions (see, e.g. [4] and references therein).

Analyzing the DFT results [3] we managed to extract the main interactions responsible for the chain structure formation in SiO/Pd(111) system. This is possible if to compare the formation energies of various low-energy structures obtained from DFT calculations to the energies of these structures given by lattice-gas expansion

of the energy. The calculation of interaction constants by comparison of the energies was performed, e. g. for O/Rb(0001) [5], Ag/Pt(111) [6] and O/Pt(111) [7]. Performing such a comparison to different SiO structures on Pd(111), we found that, in order to obtain the chain structures, the nearest neighbour (NN) pair interaction of two SiO complexes (v) has to be repulsive. We also found that the interaction of three SiO complexes in a line (v_t) has to be attractive and of the same order of magnitude as v . Therefore our idea was that the mechanism of stripe formation in SiO/Pd(111) system might be governed by competition of these two main interactions. This model is quite unusual for stripe formation, because it neglects the longer-range interaction (v_t attraction is responsible only for intrachain formation). It is known [8] that formation and thermodynamical stability of the most simple 2D stripe structure 2:1 (alternating rows of filled and empty chains) along with repulsion at NN sites also requires at least the repulsion at next-NN sites at particle coverage 0.5.

Here, using kinetic Monte Carlo (KMC) calculations, we demonstrate that the (2×1) stripe phase can exist in a model with two competing interaction parameters, NN repulsion and attractive trio interaction in a chain, i.e. without effects of long-range forces. The formation of this thermodynamically metastable stripe structure is caused by kinetic effects. Despite higher formation energy and due to a

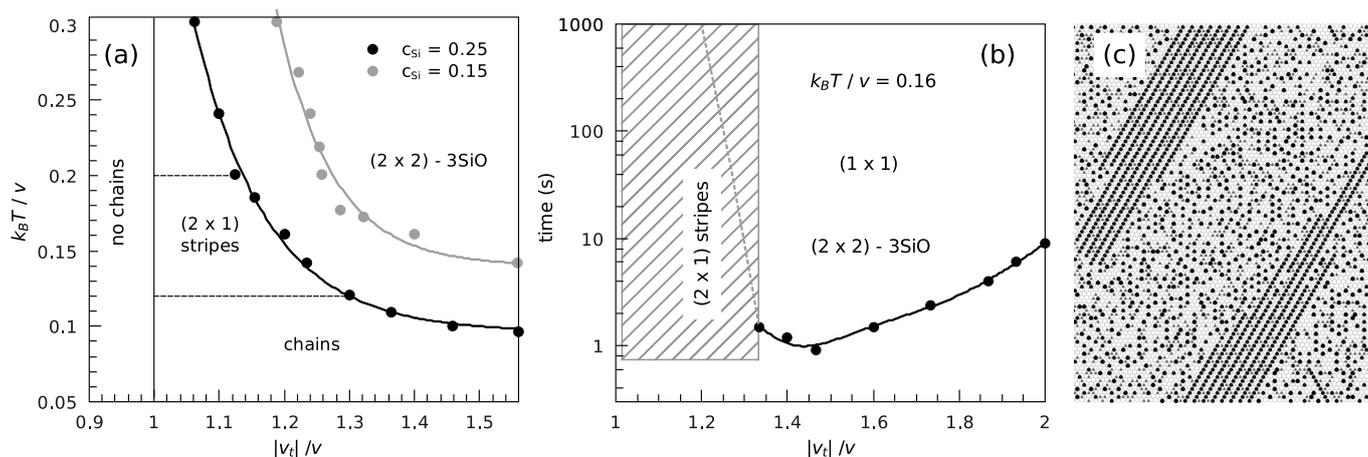


Figure 1 (a) Phase diagram obtained after 10 s at diffusion and reaction rates equal to 10^5 s^{-1} , $c_O = c_{Si} = c_{H_2} = 0.25$ and $v_1(H_2 - O)/v = 1.3$. To avoid intersections horizontal and vertical lines defining (2×1) phase are not shown for $c_{Si} = 0.15$. In that case (2×1) region gets narrower. (b) Time of (2×1) stripe structure stability (dashed region) and time of (2×2) structure formation from chains at $k_B T / v = 0.16$. The transition is not sharp, so the results obtained in between (2×1) and (2×2) phases (gray line in dashed region) is approximate. (c) Snapshot of (2×1) structure at $|v_t| / v = 1.13$ and $k_B T / v = 0.16$ after 1000 s. Black dots correspond to SiO complexes.

high potential barrier, such a structure can exist for a long time in a particular region of interaction parameters. In a case of surface strains and defects which can stabilize such domains, the time of stripe existence can become infinite and therefore such structures can be found in SiO/Pd(111) system.

2 Model Our simulations are performed on a hexagonal (111) lattice of 96×96 sites with periodic boundary conditions. Silane decomposition is modelled by random Si and H_2 deposition on the lattice initially populated by oxygen atoms. We maintained the experimental conditions [2] assuming that all constituents, Si, O, and H_2 , diffuse over fcc sites of the hexagonal lattice, and O and Si coverages (population of fcc sites) are $c_O = 0.25$ and $c_{Si} = 0.1-0.25$. Though hydrogen is also mostly located at fcc sites, it often occupies other positions and even dissolves to subsurface [9,10]. Therefore for simplicity we assumed that it remains in a molecular form, and the coverage of H_2 on fcc sites is a parameter of the model.

The KMC simulations are performed using the standard model and pair algorithm approach [11, 12]. The main idea of the algorithm is to consider two NN sites simultaneously and account for all possible processes therein. The processes considered in our simulation are Si, O, and H_2 diffusion via NN fcc sites and Si+O and H_2 +O reactions leading to formation of the SiO complex on a single site and formation of water (which is immediately removed from the surface) respectively. The SiO complex can diffuse over fcc sites and form -SiO-SiO-... chains. It should be noted that diffusion rates crucially depend on particle interaction which modify the hopping rates. Though reaction rates are constant, the particle interaction affects the probability to find particles in NN sites required for reac-

tion, and this implicitly affects the reaction rates. Initially the calculations were performed when all diffusion and reaction rates are 10^5 s^{-1} . As obtained from the DFT and lattice-gas comparison, we assumed that there exists repulsion v_1 between all possible NN pairs of Si, O, and SiO, except the case of repulsion of two SiO complexes which is $v = 2v_1$, since Si-Si and O-O repel each other on a lattice and top level. H_2 molecules are assumed to interact only with NN O atoms. Though this approximation is rather simple for quantitative description of silane decomposition on Pd(111), it demonstrates the most characteristic features of stripe structure formation.

3 Results Finite one-dimensional chains with the energy $E_{1D} = (v - |v_t|)$ per SiO complex are initially formed at $v < |v_t|$, and they are the first building blocks for other phases. The stability of these phases is rather different. In Fig. 1a we present the phase diagram ($k_B T / v$ vs $|v_t| / v$) taken after 10 s. We have found that there exists a specific region of interaction parameters at $|v_t| \gtrsim v$, where (2×1) stripe structure (Fig. 1c) is obtained. The most surprising result is that the energy of this 2D phase, $E_{(2 \times 1)} = E_{1D}$, i.e. the occurrence of (2×1) structure does not require the inclusion of longer-range forces. It should be noted that in our model two other phases with even lower energy can be formed: the transient “honeycomb-triangle” (2×2) -3SiO phase (further denoted as (2×2)) with domain occupancy $c_{SiO} = 0.75$ and energy $E_{(2 \times 2)} = 2(v - |v_t|)$, and the “ferromagnetic” (1×1) structure with $E_{(1 \times 1)} = 3(v - |v_t|)$ which has all NN fcc sites occupied. Only (1×1) phase is a thermodynamically stable structure gradually obtained from the (2×2) one.

What is the reason of the (2×1) phase occurrence in our model? The region at $|v_t| \gtrsim v$ is characterized by eas-

ily nucleating and disintegrating chains. At high enough temperature the formation of (2×1) structure from separate chains occurs in 0.1-10 s time limit. The chains kinetically favour parallel orientation. This is because frequent encounter of unparallel chains at repulsive v leads to their easy disintegration at $|v_t| \gtrsim v$ and gradual formation of parallel structure. However, it is more difficult to understand why they maintain the compact 2D (2×1) stripe structure shown in Fig. 1c. Our idea is that in this way the system tries to avoid for the separate SiO complexes to get in between the chains, since inclusions would increase the energy of (2×1) domain. Thus, when the number of free SiO considerably exceeds the number of SiO in chains, the compact (2×1) structure is kinetically obtained due to an "internal pressure" created by diffusion of free SiO complexes. Increase of v_t leads to higher concentration of SiO complexes participating in (2×1) or (2×2) domain formation. Since the concentration of (2×2) phase is higher than that of (2×1) , the increase of local concentration of SiO complexes promotes the formation of (2×2) phase at $|v_t|/v \gtrsim 1.2$. On the other hand, the increase of v_t makes the chains more resistant to disintegration, and therefore the process of (2×2) phase formation from chains at high v_t and especially at low temperature might be quite long.

In spite of higher energy, (2×1) structure is very stable at its region of the diagram. This means that local potential barrier separating this phase and (2×2) structure is very high. We performed the calculations up to hours, and (2×1) structure survived as is seen in Fig. 1b,c. It should also be noted that occurrence of (2×1) stripe structure is not related to presence of hydrogen in this system and impact of H_2+O reaction. This structure is formed even when $c_{H_2} = 0$.

In order to confirm the tendency to compactness and stability of stripe domain, we performed also the calculation with included next-NN repulsion v_2 at a distance $\sqrt{3}a$ (though at the moment we have no clues that this interaction is relevant for SiO/Pd(111) system). Due to this interaction the interchain distance increases from $2a$ to $3a$, but not further. The chains become shorter and they form small domains of (3×1) stripe structure of coverage 0.33. The repulsion v_2 prevents the occurrence of 120 degree angles between chains which are the main nucleation centers for (2×2) phase formation: there is an energy gain when SiO particle connects two chains at this angle in a model without v_2 . Note, that for higher values of v_2 the stripe structure (3×1) can become thermodynamically stable phase.

Decrease of Si coverage leads to shift of (2×1) phase region on the phase diagram to higher values of v_t : due to deficiency of SiO the formation of chains at $c_{Si} = 0.15$ starts at $|v_t| > v$, and the transformation to (2×2) structure begins only when sufficient coverage of SiO complexes in chains is achieved - at higher values of $|v_t|$ than for $c_{Si} = 0.25$ (see Fig. 1a). Visually (2×1) stripe structure close to (2×2) border at $c_{Si} = 0.15$ develops into longer, but more narrow domain pattern than that at $c_{Si} = 0.25$,

though the coverage of SiO participating in domain formation is almost the same.

The increase of c_{H_2} has the same effect on stripe formation as decrease of c_{Si} , if both reaction rates (Si+O and H_2+O) are equal. The increase of c_{H_2} leads to redistribution of oxygen atoms for the both reactions. When there are more H_2 molecules, the probability of H_2+O reaction is higher. As a result, less SiO complexes is being left for the stripe formation, and the stripe domain size is smaller.

Decrease of reaction rates in comparison to diffusion rates also has its effect for stripe formation and (2×1) region in the phase diagram. Decrease by 2-3 orders of magnitude still generates typical (2×1) patterns. But lower reaction rates lead to fast formation of (2×2) phase in (2×1) region of Fig. 1a. This is because both reactions promote the occurrence of empty sites. The decrease of reaction rates stimulates total increase of particles on a lattice, more useful for (2×2) phase formation.

In conclusion, by comparing the formation energies we have determined two main interactions necessary for stripe formation during silane decomposition on oxidized Pd(111). Using kinetic Monte Carlo method we have demonstrated that the simplest stripe structure (2×1) can occur in the model *without* longer-range interactions. Despite higher energy, this thermodynamically metastable structure can exist for times exceeding the time of experiment. Time of (2×1) existence might be also extended due to surface strains and defects of Si+O+H system on Pd(111).

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References

- [1] D. C. Kershner and J. W. Medlin, Surf. Sci. **602**, 786 (2008).
- [2] D. C. Kershner, W. Zhang, and J. W. Medlin, Surf. Sci. **602**, 3225 (2008).
- [3] D. C. Kershner, M. P. Hyman, and J. W. Medlin, Surf. Sci. **602**, 3603 (2008).
- [4] A. Joknys and E. E. Tornau, J. Magn. Magn. Mater. **321**, 137 (2009).
- [5] C. Stampfl, H. J. Kreuzer, S. H. Payne, H. Pfnur, and M. Scheffler, Phys. Rev. Lett. **83**, 2993 (1999).
- [6] K. A. Fichthorn and M. Scheffler, Phys. Rev. Lett. **84**, 5371 (2000).
- [7] A. P. J. Jansen and W. K. Offermans, J. Comput. Methods Sci., Eng. **2**, 351 (2002).
- [8] W. Kinzel, W. Selke, K. Binder, Surf. Sci. **121**, 13 (1982).
- [9] R. Löber and D. Hennig, Phys. Rev. B **55**, 4761 (1997).
- [10] T. Mitsui, M. K. Rose, E. Fomin, D. F. Ogletree, and M. Salmeron, Surf. Sci. **511**, 259 (2002).
- [11] G. Zvejnieks and V. N. Kuzovkov, Phys. Rev. E **63**, 051104 (2001).
- [12] E. E. Tornau, V. Petrauskas, and G. Zvejnieks, Catalysis Today **116**, 62 (2006).