Model for hydrogen-induced Sb atoms reconstruction
$\sqrt{3} \times \sqrt{3} \rightarrow 2 \times 1$ on Si(111)

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Abstract. We propose the 6-state model to describe the hydrogen-induced $\sqrt{3} \times \sqrt{3}$ (trimers) $\rightarrow 2 \times 1$ (zigzag chains) reconstruction in 1 ML Sb/Si(111) system. In agreement with recent experimental data, we demonstrate that adsorption of small coverage of hydrogen atoms turns the $\sqrt{3} \times \sqrt{3}$ phase into mixed $\sqrt{3} \times \sqrt{3}$ and $2 \times 1$ structure. The length and number of zigzag chains grow with the increase of hydrogen concentration.

1. Introduction
The domains of three Sb-formed reconstructions ($\sqrt{3} \times \sqrt{3}$ [1, 2, 3, 4, 5], $2 \times 1$ [6] and $1 \times 1$ [5]) have been observed on Si(111) surface at Sb saturation coverage of 1 ML. Usually patches of accompanying phases are obtained in the main phase and this depends on preparation conditions – initial Sb coverage, its flux rate and substrate temperature. The STM experiments [4] and first principles ab initio calculations [3, 7, 8, 9] show that in all ordered Sb/Si(111) structures Sb atoms prefer the positions on top of the first layer Si atom. However in both $\sqrt{3} \times \sqrt{3}$ and $2 \times 1$ structures Sb atoms are slightly shifted from the ideal on top position as shown in Fig. 1. In $\sqrt{3} \times \sqrt{3}$ three neighbouring Sb atoms move towards mutual center on top of the second layer Si atom in the so-called $T_4$ site and form trimers (milk-stool model). In $2 \times 1$ phase Sb atoms form zigzag chains.

The formation energies of the $\sqrt{3} \times \sqrt{3}$ and $2 \times 1$ phases are very similar in all mentioned 1 ML Sb covered systems. This was recently confirmed by the experiment [4] where it was demonstrated that small amounts of atomic hydrogen adsorbed on $\sqrt{3} \times \sqrt{3}$-Sb/Si(111) phase partly reconstruct it into the H-2 × 1-Sb/Si(111). We propose that this reconstruction could be regarded as the phase transition which is described by the 6-state model. Here we present this model for the 1 ML Sb-Si(111) system and also demonstrate how small concentrations of hydrogen can induce experimentally observed $2 \times 1$ ordering in the $\sqrt{3} \times \sqrt{3}$ phase.

2. Model
We denote the Sb atom states (shifts) on Si(111) in a way shown in Fig. 1. Then the Hamiltonian (per Sb atom) of our 6-state model has the form

$$H = \frac{1}{2} v_{i,j} \delta(p_i, q_j) - \frac{1}{3} v_{i,j,k} \delta(p_i, q_j, r_k),$$

(1)
where $\delta(p_i, q_j)$ is Kroneker delta function equal to 1 when combination of states $p_i$ and $q_j$ in the nearest neighbor Sb sites $i$ and $j$ corresponds either to $\sqrt{3} \times \sqrt{3}$ or $2 \times 1$ phases and zero otherwise, and

\[
v_{i,j} = \begin{cases} v_{\sqrt{3} \times \sqrt{3}}, & \text{if } (p_i, q_j) = (1, 3), (3, 5), (5, 1) \\ v_{2 \times 1}, & \text{if } (p_i, q_j) = (1, 4), (2, 5), (3, 6) \end{cases}
\]

\[
v_{i,j,k} = v_t, \quad \text{if } (p_i, q_j, r_k) = (1, 3, 5).
\]

Actually, the Hamiltonian (1) consists of two competing parts: the part responsible for occurrence of the $\sqrt{3} \times \sqrt{3}$ phase trimers, represented by attractive pair interaction $v_{\sqrt{3} \times \sqrt{3}} > 0$ and triple interaction $v_t > 0$, and the part stimulating the occurrence of the zigzag chains of the $2 \times 1$ phase represented by attractive pair interaction $v_{2 \times 1} > 0$. The interaction parameter $v_t > 0$ contribute only for the $\sqrt{3} \times \sqrt{3}$ phase. Three pairs of the $v_{2 \times 1}$ term are due to the fact that $2 \times 1$ zigzag chains in hexagonal lattice can run in three possible directions possessing $(1,4)$, $(2,5)$ and $(3,6)$ states. Calculation of phase transitions with the energy (1), (2) and $v_t = 0$ shows that the $\sqrt{3} \times \sqrt{3}$ phase is promoted, if $v_{\sqrt{3} \times \sqrt{3}} > v_{2 \times 1}$, but the $2 \times 1$ phase is more favorable, if $v_{\sqrt{3} \times \sqrt{3}} < v_{2 \times 1}$. In our simulations we assume that $v_{2 \times 1} > v_{\sqrt{3} \times \sqrt{3}}$, but $v_{2 \times 1} \approx v_{\sqrt{3} \times \sqrt{3}} + v_t/3$ and for simplicity take $v_t = v_{\sqrt{3} \times \sqrt{3}}$.

**Figure 1.** Schematic representation of (a) $\sqrt{3} \times \sqrt{3}$ phase and (b) fragments of the 3-fold zigzag 2 $\times$ 1 chains with indicated Sb states (shifts) on Si(111). Arrows and numbers denote the shift of Sb atom from the center of the top layer Si atom. (c) Scheme of how hydrogen atom breaks one of two Sb-Sb bonds and cancels the interaction constant on that bond.

For calculations by Monte Carlo method (Metropolis algorithm) we use hexagonal lattice of 48 $\times$ 48 Sb sites. The phase transitions from both ordered phases ($\sqrt{3} \times \sqrt{3}$ and $2 \times 1$) to high-temperature disordered phase (with probability of each state approximately equal to 1/6) are calculated [10] for different values of the ratio $v_{2 \times 1}/v_{\sqrt{3} \times \sqrt{3}}$. Phase transition temperature $T_c$ is determined from the peak of temperature dependence of specific heat and phase diagram is obtained when there are no hydrogen atoms on the surface.
Figure 2. (a) Temperature dependences of order parameters $\eta_{\sqrt{3}\times\sqrt{3}}$ and $\eta_{2\times1}$ at $v_{2\times1}/v_{\sqrt{3}\times\sqrt{3}} = 1.21$ and hydrogen coverage $c_H = 0$, 0.1 and 0.2. (b) Dependence of order parameters $\eta_{\sqrt{3}\times\sqrt{3}}$ and $\eta_{2\times1}$ at $T \to 0$ on $c_H$ for different distances from the boundary of $\sqrt{3} \times \sqrt{3}$ and $2 \times 1$ phases: $v_{2\times1}/v_{\sqrt{3}\times\sqrt{3}} = 1.21$ (1), 1.15 (2) and 0.99 (3).

3. Effect of hydrogen adsorption

Evaporation of 3 ML of Sb at 650 – 670 C and further desorption leads to formation of 1 ML $\sqrt{3} \times \sqrt{3}$-Sb/Si(111) structure [3, 4, 5] which is the most often observed phase on 1 ML Sb/Si(111) surface. However, large areas of the zigzag chains corresponding to the $2 \times 1$ pattern are found when hydrogen atoms are additionally adsorbed on $\sqrt{3} \times \sqrt{3}$-Sb/Si(111) [4].

In order to simulate this experiment using the model (1), we distribute hydrogen atoms randomly in the $\sqrt{3} \times \sqrt{3}$ structure. The interaction parameters are chosen in the $\sqrt{3} \times \sqrt{3}$ part of the phase diagram, but very close to the $\sqrt{3} \times \sqrt{3}$ and $2 \times 1$ phase boundary. This choice is justified, since both phases have very similar surface formation energy [7]. We assume that a hydrogen atom randomly breaks one of two Sb-Sb bonds when adsorbed close to Sb atom (as shown in Fig. 1c) and cancels the interaction corresponding to the broken bond. If the broken bond belongs to the $\sqrt{3} \times \sqrt{3}$ trimer, the local energy increases by $v_{\sqrt{3}\times\sqrt{3}} + v_t/3$, and the two remaining $v_{\sqrt{3}\times\sqrt{3}}$ interactions of the trimer can be readily substituted by $v_{2\times1}$ interaction promoting the $2 \times 1$ ordering, if $v_{2\times1} > v_{\sqrt{3}\times\sqrt{3}}$.

In such a manner part of trimers can be substituted by zigzag chains running in one, two or three directions. In our simulations this is demonstrated by temperature dependences of order parameters $\eta_{\sqrt{3}\times\sqrt{3}} = \langle \delta(1, 3, 5) \rangle$ and $\eta_{2\times1} = \frac{1}{2}(\langle \delta(1, 4) \rangle + \langle \delta(2, 5) \rangle + \langle \delta(3, 6) \rangle)$ (see Fig. 2a).

Insertion of hydrogen atoms decreases the $T_c$ of disordered-to-$\sqrt{3} \times \sqrt{3}$ transition, weakening and smoothing the anomalies of functions characterizing this point. The length and number of zigzag chains grows with increase of hydrogen concentration $c_H$. At low $c_H$ (< 0.05) trimers possessing H-atom lose one bond, but no chains with more than 3 Sb atoms are created. When $c_H = 0.1$, large part of H-atoms are located at (or very close to) the ends of small chains. This might be seen in the snapshots of our simulation in Fig. 3. When $c_H$ is around 0.2 part of H-atoms finds itself comfortable even inside the chains as well. Actually hydrogen atoms force the zigzag chains to "freeze" inside the $\sqrt{3} \times \sqrt{3}$ environment keeping the chains "pinned" by the H-atoms.

In conclusion, we present the 6-state model to describe hydrogen-induced trimer to zigzag
The snapshots of our simulation at \( c_H = 0.05 \) (a), 0.1 (b), 0.15 (c) and 0.2 (d) for \( v_{2\times1}/v_{\sqrt{3}\times\sqrt{3}} = 1.21 \) and \( k_B T/v_{\sqrt{3}\times\sqrt{3}} = 0.01 \). Black circles – Sb atoms, small white circles – H atoms.

chains reconstruction, \( \sqrt{3} \times \sqrt{3} \to 2 \times 1 \), in 1 ML Sb system on Si(111). Our model is perfectly suited to explain the experimental data [4], since similar scheme of hydrogen-induced reconstruction was recently suggested in this paper.

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