



Phase transition of Sr on Si (001): First principles prediction and experiment

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ABSTRACT

The ability to understand and predict the phase diagrams of surface phases from first principles can be valuable for developing processes for growth of epitaxial structures. In the growth of epitaxial oxides on Si (001), a submonolayer phase of Sr plays a key role. The physical structure for this phase, which has 2×3 symmetry and occurs at $1/6$ monolayer Sr coverage, was recently elucidated using both first principles theory and diffraction experiments [J.W. Reiner, K.F. Garrity, F.J. Walker, S. Ismail-Beigi, C.H. Ahn, Role of strontium in oxide epitaxy on silicon (001), *Phys. Rev. Lett.* 101 (10) (2008) 105503.]. Our approach to understanding the broader Sr/Si phase diagram combines density functional theory with a thermodynamic analysis of the phase equilibrium between a Sr lattice gas and the 2×3 structure. We use reflection high energy electron diffraction (RHEED) to experimentally determine the phase diagram, finding good agreement with theoretical predictions.

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1. Introduction

A unique feature of the epitaxial growth of oxides on Si (001) is the formation of a reconstructed submonolayer alkaline earth metal layer (usually Sr) on the clean Si surface that occurs before deposition of the oxide itself [2]. The structure and kinetics of this phase have been the subject of much attention [3,4]. Recently, it was shown that there are two deposition paths for Sr on Si (001) which depend on the deposition temperature [1,5]. In both cases, the Si surface begins in its canonical 2×1 dimerized pattern. At temperatures from 0 °C to 400 °C, the Si is kinetically limited, and Sr adatoms bind to the valleys between Sr dimer rows. This process continues until all the low energy binding sites are filled at $1/2$ ML, and the surface still has 2×1 symmetry due to the Si dimers. On the other hand, at temperatures from 400 °C to 600 °C, Si motion is not kinetically limited. The surface again starts with 2×1 symmetry; however, as the Sr coverage is increased, an ordered 2×3 phase is observed at $1/6$ monolayer (ML) coverage, which then is replaced by a 1×2 phase at $1/2$ ML. The 2×3 structure results from a reorganization of the Si surface catalyzed by the Sr adatoms and is the thermodynamic ground state at $1/6$ ML. This

phase was identified using RHEED [2,6,1], and it has also been studied with scanning tunneling microscopy (STM) [7,8]. In our recent density functional theory work [9], we provide details of the structures which explain the RHEED data up to 600 °C as well as simulated STM images of the 2×3 structure, which are in good agreement with experiment.

Understanding of these two pathways for Sr deposition on Si (001) has provided two experimentally verified routes for creating an appropriate template layer for oxide epitaxy [1,5]. In the low temperature (0–400 °C) deposition route, the Si dimers remain in place, and the oxide is grown on a 2×1 template layer. In the high temperature (400–600 °C) route, the initial Si dimers are replaced by the 2×3 structure at $1/6$ ML, and then rearranged again into a 1×2 structure at $1/2$ ML, which also provides a template for oxide growth.

Our aim is to predict and understand the temperature-coverage phase diagram in the high temperature region, 500–800 °C (see Fig. 4), for the interesting and important Si/Sr surface system. In particular, we wish to understand the order-disorder transition near $1/6$ ML between the ordered 2×3 phase and a disordered lattice gas, which consists of Sr adatoms distributed with no long range order on top of a dimerized Si surface. In order to model the transition, we use first principles density functional theory (DFT) to analyze the surface chemistry and grand canonical Monte Carlo methods to evaluate the thermodynamics. We also use

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reflection high energy electron diffraction (RHEED) to map out the transition and show quantitative agreement with theory.

2. Lattice gas Hamiltonian

First principles results and experiments show that the ground state of Sr on Si (100) has an interesting behavior versus Sr coverage: For coverages below 1/6 ML, the Si surface is the usual 2×1 dimerized one with the Sr forming disordered chains (a lattice gas); however, at 1/6 ML the ground state changes to an ordered 2×3 structure (formed by creating dimer vacancies) [1,9]. Although not relevant to our present work, a kinetic barrier to the Si motion prevents the formation of the 2×3 structure unless the temperature is above 400 °C. In this work, we are concerned with the behavior of the surface at higher temperatures and for Sr coverages close to 1/6 ML. Therefore, it is safe to assume that the system will be in thermal equilibrium. For temperatures below 500 °C, we expect the lower energy 2×3 phase to dominate. However, as we discuss below, this phase has a very low entropy because perturbations to it cost a great deal of energy. On the other hand, while structures with Sr chains on a 2×1 surface have higher energy than the 2×3 structure, the configurational entropy for the Sr leads to a much larger entropic contribution to the free energy. Thus we expect a phase transition between the ordered 2×3 and the 2×1 lattice gas phases as temperature is raised for coverages close to 1/6 ML Sr.

Calculating the thermodynamics of dimerized Si with Sr adatoms requires sampling the canonical distribution for all the possible configurations accessible to the Sr lattice gas. Preferably, one should compute the energy of each configuration from first principles, but due to disorder and the large simulation cells required, this is impractical with current computational methods and infrastructure. Therefore, we resort to using a model lattice gas Hamiltonian which can be evaluated over many Sr configurations. The form chosen for the Hamiltonian, as well as its key parameters, are dictated from first principles results (next section), with no fitting parameters.

In our lattice gas Hamiltonian, we consider only the Sr degrees of freedom, with the surface Si remaining in a 2×1 dimerized configuration, as we find that all isolated defects of the Si surface are high in energy. For example, a Sr atom in an isolated unit cell of the 2×3 structure on an otherwise 2×1 dimerized silicon surface has a binding energy of 3.60 eV, which is significantly less favorable than the lattice gas, which has a typical binding energy 3.75 eV/Sr. The form for our model Hamiltonian H_{LG} is an anisotropic interacting coverage-dependent lattice gas model, where each Sr binding site i on the dimerized Si surface has occupancy n_i , where $n_i = 0, 1$:

$$H_{LG} = \sum_i n_i \left[\epsilon_i + \sum_{\alpha} J_{\alpha}(z_i) n_{i+\alpha} + E_i^{Si} \right], \quad (1)$$

$$z_i = \sum_{\alpha} n_{i+\alpha}. \quad (2)$$

The lattice is rectangular so each lattice site i has eight nearest neighbors, and α ranges over the intersite vectors. Specifically, for any site i with integer coordinates (x, y) , α ranges over the eight vectors $\pm(1, 0)$, $\pm(0, 1)$, $\pm(1, 1)$, and $\pm(1, -1)$. The number of occupied nearest neighbor sites for i is z_i . The nearest neighbor interactions $J_{\alpha}(z_i)$ are anisotropic. Due to rectangular symmetry, there are only three independent interactions $J_{10}(z_i)$, $J_{01}(z_i)$, and $J_{11}(z_i)$, and they depend on the local coverage (z_i) (see Fig. 1 for examples). In addition to the Sr site interaction terms, there is an additional term, E_i^{Si} , which imposes an energy cost for every instance of two Sr atoms

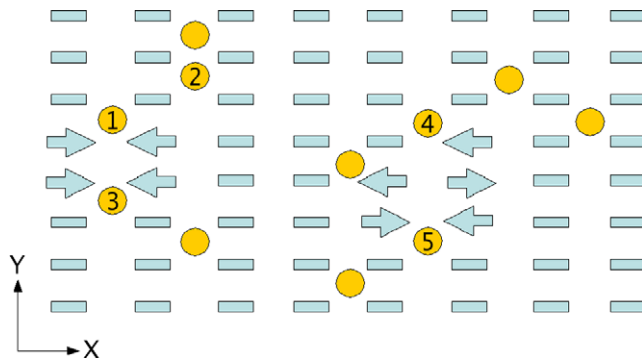


Fig. 1. Schematic top view of a typical lattice gas configuration. All Sr atoms (yellow circles) are in the A binding sites (see Fig. 2 and Section 3) between the Si dimers (light blue rectangles and arrows). The Sr labeled 1 has a single corner nearest neighbor, and the Sr labeled 2 has both a corner nearest neighbor and a nearest neighbor in the y direction. Most dimers are buckled, but are shown as flat for simplicity, and arrows are used to highlight particular buckling. The cluster of arrows on the left show dimers pinned in an unfavorable configuration by Sr atoms 1 and 3. The cluster of arrows in the center show that the dimers between Sr 4 and Sr 5 can have the more energetically favorable alternate-buckling pattern. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

with a single unoccupied site between them in y direction. The physical origin of this term is that this configuration frustrates the Si dimer buckling, as discussed below (see also Fig. 1).

In order to find the phase transition between our lattice gas model and the ordered 2×3 structure as a function of temperature and coverage, we evaluate the grand canonical partition function for the lattice gas,

$$Z = \sum_{\{n_i\}} \exp \left[- (H_{LG}[n_i] - \mu_{2 \times 3} N[n_i]) / k_b T \right], \quad (3)$$

$$N[n_i] = \sum_i n_i, \quad (4)$$

where k_b is Boltzmann's constant, T is the temperature, the sum is over all possible combinations of n_i , and the Sr chemical potential, $\mu_{2 \times 3}$, is set to the binding energy per Sr of the 2×3 1/6 ML structure. We choose $\mu_{2 \times 3}$ to be temperature independent because excitations of the 2×3 structure are much higher in energy than $k_b T$ for temperatures considered in this work (see below).

Due to the relatively long ranged and coverage-dependent anisotropic interactions in the model Hamiltonian, the grand canonical partition function cannot be summed exactly. However, this model lends itself to grand canonical Monte Carlo analysis using the Metropolis algorithm to sample the partition function [10,11]. We find that the correlation function between Sr adatoms on the surface decays exponentially with a correlation length of approximately two lattice constants at the temperatures and coverages of interest. As a result, we can safely run our calculations in a 30×30 lattice with periodic boundary conditions. We sample our partition functions until the sampling error is much smaller than all other uncertainties.

We use Monte Carlo sampling to determine, as a function of temperature, the coverage of the lattice gas in equilibrium with the 2×3 structure. This set of coverages and temperatures, which forms the phase boundary between the 2×3 structure and the lattice gas, is plotted in Fig. 4.

3. *Ab initio* calculations and parameter extraction

We use first principles theory to determine the structure and energetics of a variety of stable Sr on Si (001) configurations in order to extract the parameters for the lattice gas Hamiltonian.

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