Atomic-scale study of the adsorption of calcium fluoride on Si(100) at low-coverage regime

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We investigate, experimentally and theoretically, the initial stage of the formation of Ca/Si and Si/F structures that occurs during the adsorption of CaF$_2$ molecules onto a bare Si(100) surface heated to 1000 K in a low-coverage regime (0.3 monolayer). A low-temperature (5 K) scanning tunneling microscope (STM) is used to observe the topographies and the electronic properties of the exposed silicon surfaces. Our atomic-scale study reveals that several chemical reactions arise during CaF$_2$ deposition, such as dissociation of the CaF$_2$ molecules and etching of the surface silicon dimers. The experimental and calculated STM topographies are compared using the density functional theory, and this comparison enables us to identify two types of reacted structures on the Si(100) surface. The first type of observed complex surface structure consists of large islands formed with a semiperiodic sequence of 3 × 2 unit cells. The second one is made of isolated Ca adatoms adsorbed at specific sites on the Si(100)-2 × 1 surface.

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I. INTRODUCTION

Controlling the thickness, morphology, homogeneity, and purity of epitaxial ultrathin layers on semiconductors is of crucial importance in many domains, including nanoelectronics,1 light-emitter architectures,2 and in the fabrication of nanophotonic structures.3 In particular, the use of thin insulating layers of CaF$_2$ on Si(111) in the design of three-dimensional electronic devices4 has led to many experimental5 and theoretical6 investigations into its growth in the past 20 years. More recently, the study of the formation of CaF$_2$ structures on Si(100) surfaces has come to prominence.7–11 While for the Si(111) surface, the formation of isotropic CaF$_2$ islands is readily achieved, the Si(100) surface offers the possibility for growth of long fluorite stripes with good electronic insulating properties.11 In both cases, investigations of these substrates have shown the crucial importance of a deep understanding of the growth processes in order to achieve their control and develop new applications at the nanoscale.12 However, whereas the formation of the CaF$_2$/Si(111) interface is well documented, the initial stage of the wetting layer formation on Si(100) is still poorly understood at the nanoscale. This is particularly true for low-coverage rates and for substrate temperature above 900 K, i.e., outside the Volmer-Weber regime.

In this paper, we focus our investigations on the initial stage of the formation of the wetting layer at low coverage (0.3 monolayer [ML]) and other related products when a bare Si(100) surface heated at 1000 K is exposed to CaF$_2$ molecules. For this purpose, we use a low-temperature (5 K) scanning tunneling microscope (STM) to investigate the atomic structure of the first step of Stransky-Krastanov island growth. Our experiments reveal two main types of surface structures. One of them is built with a repeated unit cell semiperiodically arranged on the surface consisting of one missing silicon dimer replaced by a single Ca atom together with a silicon dimer having two Si-F bonds. The second structure consists of single Ca adatoms regularly localized on top of the silicon surface. Our theoretical investigations performed using the density functional theory (DFT) along with calculation of STM topographies confirm our experimental observations and allow clarification of the observed surface structures at the atomic scale.

II. EXPERIMENTAL AND THEORETICAL METHODS

For these experiments, we use n-doped (As, $\rho = 0.004 \, \Omega \cdot \text{cm}$) silicon samples prepared in ultrahigh vacuum (2.0 × 10$^{-11}$ torr). Following the cleaning and the reconstruction processes of the bare Si(100) surface,13 the sample is transferred into the STM to check its 2 × 1 reconstruction and especially the presence of a relatively low number of defects.14 The CaF$_2$ molecules used for these experiments are evaporated from small fluorite crystals (Goodfellow) using a graphite effusion cell (MBE-Komponenten) heated to ~1330 K. Throughout the evaporation process, the crucible holder is cooled by an external water flow to optimize the control of its temperature. The flux of the CaF$_2$ molecular beam is calibrated before each evaporation with a quartz microbalance. This calibration leads to a covering rate of ~1 Å min$^{-1}$. Following the calibration, the bare silicon surface is extracted from the STM and placed at ~10 cm from the effusion cell, in replacement of the quartz balance. With this procedure, we can precisely direct the molecular beam onto the silicon surface. Then, the silicon surface is set at a constant temperature of ~1000 K by resistive heating. Following these preparations, the silicon surface is exposed to the CaF$_2$ molecular beam for 15 seconds at a base pressure of ~7 × 10$^{-11}$ torr, which corresponds to a surface coverage of ~0.3 ML.11 The silicon sample is then cooled down to 12 K and transferred into the STM to be analyzed. Our results are the repeated analysis of five different samples and STM tips.

The theoretical calculations are performed using the plane-wave basis Vienna ab-initio simulation package (VASP)15,16 implementing DFT and the generalized gradient approximation (GGA) by Perdew, Burke, and Ernzerhof (PBE).17 We describe the Si-[Ne], F-1s$^2$, and Ca-[Ne] 3s$^2$ core electrons...
with projector-augmented wave (PAW) potentials. Using a cutoff kinetic energy of 400 eV and a Monkhorst–Pack k-point mesh with a separation of 0.02 Å⁻¹, we converge the total energy to values below 1 meV/f.u. (f.u. = formula unit Si-fcc). The ionic optimizations are performed until all the forces on relaxed atoms are below 0.01 eV Å⁻¹.

We first optimize the bulk Si-fcc structure with a predicted lattice constant of 5.43 Å. From this structure, we build the Si(100) surface using periodic slabs, five layers thick, separated by 15 Å along the (100) axis. The Si atoms at the bottom layer are passivated with hydrogen, and this Si-H layer is kept frozen during all the relaxations. We model the Ca adatoms on the Si(100) surface with a 5 × 4 Si(100) slab, while the Ca-F/Si(100) interface is more accurately described with a 3 × 2 Si(100) slab. The second step of our theoretical work consists of computing constant-current mode STM images and the line scans for the aforementioned slabs. For this purpose, we use the Tersoff-Hamann approximation as implemented in the bSKAN code. It employs the real-space single-electron wave functions of the slabs computed previously with VASP.

### III. RESULTS AND DISCUSSIONS

As explained in the previous section, the bare surface of the Si(100) 2 × 1 is initially observed with the STM to check the presence of a low rate of surface defects (usually less than 1%, Fig. 1(a)) prior to each CaF₂ evaporation. After the CaF₂...
exposure, the occupied state STM topographies (Fig. 1(b)) show two types of new features. As observed in Figs. 1(b) and 1(c), the silicon surface is covered with dark areas (type-A), which are structured like a discontinuous arrangement of small unit cells. They are formed in alignment with respect to the silicon dimer row orientation. Smaller bright features (type-B) are also observed on the silicon surface and are located beside the features of type-A [Figs. 1(b) and 1(c)]. A closer look at these structures allows the observation of their internal arrangement in more detail (Figs. 1(c) and 1(d)). For example, the dark areas of type-A appear to be fabricated with elements arranged quasiperiodically, while a single element of the bright features of type-B appears to be precisely located in between the silicon dimer rows (Figs. 1(d)). Note the buckling of the neighbor silicon dimers observed nearby the single bright features of type-B (Fig. 1(d)), which usually indicates a weak bonding between an adsorbate and the Si(100) surface.22,23

Figure 2 presents a deeper analysis of both structures via the measure of various relative height profiles. The relative averaged heights measured along p1 to p3 are reported in Figs. 2(b) to 2(d) and are representative of observations from all the tested samples. The profile p1 in Fig. 2(b) measured along the silicon back-bonds row and crossing the features of type-B reveals a protrusion on the buckled silicon surface with a relative height of ∼0.6 Å (Vs = −2 V). The measure of the relative distance between the two buckled silicon dimers that are adjacent to the bright feature of type-B is 19.3 Å, and this represents the distance separating five consecutive silicon dimers, i.e., 3.85 Å × 5. From Fig. 2(b), we can observe that the feature of type-B is located at the middle of this distance (9.6 Å), i.e., 2.5 × 3.85 Å.14 This indicates that the bright feature is positioned in the silicon back-bonds and in between two silicon dimers. This is confirmed by a comparison of the STM topographies in the occupied and unoccupied states (Figs. 2(e) and 2(f)). The profile p2 in Fig. 2(c), measured on the same protrusion across the dimer rows, reveals that the distance between the two observed bright features is ∼15 Å, which is consistent with the distance separating two silicon back-bonds rows. However, the profile p3, measured along a silicon dimer row surrounding a feature of type-A, reveals an apparent height of this structure located 0.7 Å below the silicon surface, which is materialized here by the unbuckled silicon dimer row.

We now concentrate on the structure of type-B. As will be discussed later in the paper, and as previously reported,11 one can anticipate that several Ca atoms resulting from the dissociation of CaF2 molecules will be adsorbed onto the silicon surface. Considering the previous experimental observations, our theoretical investigation allows us to test a configuration that corresponds to a single Ca adatom located in between the silicon dimer rows and between two silicon dimers as described in Fig. 3(a). The ensuing calculated STM topographies (Figs. 3(b) and 3(d)) can be compared with the experimental STM topographies of the features of type-B observed on the Si surface with a very reasonable agreement (Figs. 3(c) and 3(e)). Indeed, our calculations reproduce clearly both the occupied state (Figs. 3(b) and 3(c)) and the unoccupied state (Figs. 3(d) and 3(e)) STM topographies. A series of calculated STM images can be compared with experimental topographies at various surface voltages (Fig. 3(f)). The slight differences observed in the
 derived with precision. In particular, we can observe that the internal structures of type-A are mainly oriented in a head-to-tail (HTT) disposition (see blue arrows in Figs. 4(a) and 4(b)). The occupied state STM topographies for V_s ranging from −1.5 to −2.5 V (Fig. 4(d) to 1(f)) reveal similar internal structural arrangement. In addition to these STM topographies, the electronic properties of these structures can also be characterized. For this purpose, we perform several differential conductance (dI/dV) spectra measurements on both the surface and at various locations inside the dark areas. The ensuing dI-dV curves are averaged for each area, and the final curves are representative of reproducible measurements. The corresponding spectra are shown in Fig. 4(g), and they reveal that the surface gap is slightly enlarged when the dI-dV measurements are performed on the dark structures compared to the bare silicon surface, in particular for V_s ranging between 0 and +1 V. This difference mainly concerns the unoccupied π* surface states, which are delocalized along the coupled Si dimers of the silicon dimer rows. This suggests that coupled Si dimers do not exist anymore in the type-A areas, most probably due to the chemical reaction of CaF_2 molecules with the silicon surface.

A detailed comparison of the occupied (Fig. 5(a)) and unoccupied (Fig. 5(b)) state STM topographies of the features of type-A enables us to define a unit cell (red rectangles). The position of the unit cells on the Si surface is determined from the position of the silicon dimers of the bare surface (white circles in Figs. 5(a) and 5(b)). Each unit cell can be repeated, with a particular orientation, to form the observed reconstructed dark area. Consequently, we can observe that the entire incoming CaF_2 components to be present in the unit cell in a symmetrical way. In Fig. 6, we display the unoccupied (V_s = +2, 1.2, and +1 V (Figs. 4(a) to 4(c)) reveal a quasiperiodic internal structure. The internal elements of the dark areas are arranged along the dimer rows to build structures of various sizes, ranging from one to several dimer rows on the silicon surface. An STM topography is acquired at V_s = +1.0 V to show the p(2 × 2) buckled reconstruction of the adjacent silicon dimers. From this, the location of the Si dimers and the internal structure of type-A areas can be
FIG. 5. (Color online) (a) and (b) 115 × 115 Å² occupied (\(V_s = -1.5 \text{ V}, 61 \text{ pA}\)) and unoccupied (\(V_s = +2.0 \text{ V}, 61 \text{ pA}\)) STM topographies of a type-A area, respectively. The red rectangles define the unit cells. The white circles indicate the positions of the silicon dimers on the bare surface. The green rectangles define the selected zone of the 15.4 × 15.4 Å inserts.

FIG. 6. (Color online) (a) and (c) Comparison of the experimental STM topographies (inserts of Fig. 5) and the calculated STM topographies for the occupied states (\(V_s = -1.5 \text{ V}, V_{\text{theo}} = -1.0 \text{ V}\)) and unoccupied state (\(V_s = +2.0 \text{ V}, V_{\text{theo}} = +1.0 \text{ V}\)), respectively. The calculated images were performed with the 3 × 2 Si(100) supercell in which the blue atoms are Si, the green atom is Ca, and the turquoise atoms are F. The doted black/white lines are guidance for the eyes to show the silicon dimer location (light-gray circles). (b) and (d) Comparison between theoretical and experimental averaged profiles along the A-A′ and B-B′ sections taken from (a) and (c), respectively. (e) Comparison between observed and computed STM images for a series of bias voltages \(V_s = -2.0, -1.5, +1.0, +1.6, \text{ and } +2.0 \text{ V}, \) and \(V_{\text{theo}} = -1.0, -0.5, +0.2, +0.6, \text{ and } +1.0 \text{ V}\).
focused on the dynamics of the CaF₂ reactivity on the Si(100) surface, we can draw a simple scenario for the fabrication of the observed unit cell if we assume that the Si(100) surface is etched similarly with F₂ or CaF₂ molecules. Therefore, we assume that, preliminary to the silicon etching process with CaF₂, the silicon surface requires a passivation of the silicon dimer with F atoms according to the etching process with F₂ molecules such that:

\[ 2\text{Si} + \text{CaF}_2 \rightarrow \text{Ca} + 2\text{SiF}_2. \]  

(1)

Thus, to etch a silicon dimer, at least four F atoms are needed to form two desorbing SiF₂ molecules. Consequently, a minimum of two CaF₂ molecules is required for this process, such as:

\[ 2\text{Si} + 2\text{CaF}_2 \rightarrow \text{Ca} + 2\text{SiF}_2 + \text{CaF}_2 \rightarrow 2\text{Ca} + 2\text{SiF}_2. \]  

(2)

Following Eq. (2), the two remaining Ca atoms might stay adsorbed on the silicon surface. One of these Ca atoms can be used to fill the missing dimer, while the remaining Ca atoms can either contribute to the fabrication of the observed structures of type-B or desorb from the silicon surface. The process in Eq. (1) can be repeated on the silicon dimers adjacent to the removed silicon dimer to ultimately produce the unit cell with two Si-F bonds, as described previously. However, as observed in our work, the etching process of the Si(100) surface during the deposition of CaF₂ molecules is periodic (one silicon dimer is removed every three dimers of the same dimer row), contrary to what is observed in the presence of fluorine gas, which allows continuous lines of silicon vacancies to be engraved. Thus, the etching of the silicon surface with CaF₂ molecules seems to occur in a different way and restrains the formation of continuous lines of silicon dimer vacancies. The presence of the Ca atom in replacement of the etched dimer in the unit cell might be related to this process. Additionally, we have observed that the relative dispositions of the unit cells in the HTT structure are shifted to produce the formation of adjacent lines of Si-F dimers (see Fig. 7). This configuration is consistent with a passivation process of Si dimers with F atoms prior to the silicon etching. Therefore, the formation of Si-F bonds might also occur at lower coverage rates during CaF₂ exposure. The etching process of the silicon dimer and, therefore, the complete formation of the observed type-A areas require additional CaF₂ molecules, which explains the numerous Ca adatoms forming the observed features of type-B.

IV. CONCLUSION

We have performed the first atomic-scale study of wetting layer formation when the Si(100) surface is exposed to CaF₂ molecules at low coverage (~0.3 ML). This results in the formation of two types of reacted surface structures. The first one is observed as a complex reconstruction involving a regular arrangement of 3 x 2 unit cells formed with one adsorbed Ca atom and two Si-F bonds. The second structure is made of single Ca adatoms adsorbed on the Si(100) surface. We have shown that both structures result from the dissociation of the CaF₂ molecules when adsorbed on the Si(100). Subsequently, the dissociation of the CaF₂ induces the etching of the silicon surface. The characterization of these observed reacted structures is supported by DFT calculations of their surface geometry and STM topographies. This work emphasizes the high-precision analysis offered by the STM methods to investigate the initial-stage formation of ultrathin layers, especially when they are performed at low temperature and combined with DFT calculations. Finally, this work will provide insight for studying the growth of insulating layers on Si(100) at the atomic scale, in particular for the formation of one-dimensional parallel stripes in higher coverage regimes.

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ATOMIC-SCALE STUDY OF THE ADSORPTION OF...

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