

Role of doping in probe microscopies for the Si(111) 7×7 surface

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We investigate a scanning probe microscopy image flickering phenomenon, i.e., distinct changes in intensity with the tip height, observed on a B-doped Si(111) 7×7 reconstructed surface. The phenomenon is exclusively observed in heavily doped systems owing to large variations in the adatom heights (~ 0.5 a.u.) and the existence of *bistable* subunits upon doping as the probe tip approaches the surface. We find that B atoms prefer to reside in the surface layer, which is ~ 1.1 eV more stable compared to interior layers. These dopant atoms exert a substantial influence on the structural integrity and electronic structure of the lattice.

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Silicon is indispensable for creating advanced electronic components. It is abundant, forms a stable oxide, and one can exercise precise control over its electrical properties and microstructure. As a consequence, silicon is a material whose fundamental properties have been extensively explored [1]. For example, the Si(111) 7×7 reconstructed surface has garnered notable attention since its discovery over a half-century ago through a low-energy electron diffraction experiment [2]. The complexity of this surface for an elemental material is unusual, and despite silicon being a semiconductor in bulk, the reconstructed surface exhibits metallic properties [3].

This complex surface is considered a touchstone for assessing the feasibility of scanning probe microscopes. Extensive experimental and theoretical research work [4–15] has been performed to characterize the surface structure. Two years after the reconstructed surface was imaged by scanning tunneling microscopy (STM), the dimer-adatom-stacking-fault

(DAS) model was proposed by Takayanagi *et al.* [13,14]. The DAS model accounts for the observed structural features and aligns with theoretical computations that establish it as energetically favorable. More recently, atomic force microscopy (AFM) has been applied to this silicon surface [4]. AFM and STM are now widely used experimental instruments for visualizing nanoscale surfaces and molecules with atomic resolution [14–32]. With the most sensitive type of AFM, the frequency modulation mode [33], weak interactions are measured between a vibrating probe tip and the specimen of interest, and changes in the frequency of the probe oscillation are measured for generating images. For STM, images are generated based on the magnitude of the quantum tunneling current between the tip and the specimen.

Figure 1(a) illustrates the DAS model of the intrinsic Si(111) 7×7 reconstructed surface. Through the introduction of different numbers of B dopants, this surface symmetry can be disrupted. We divide the four adatom classes into a dozen entries using the following notation: top (t), middle (m), and bottom (b). Figure 1(b) shows an AFM image of a pure Si surface. The tip-sample distance is relatively small, indicated by the positive frequency shift of up to $+7.5$ Hz and the slight irregularity in the adatom images,

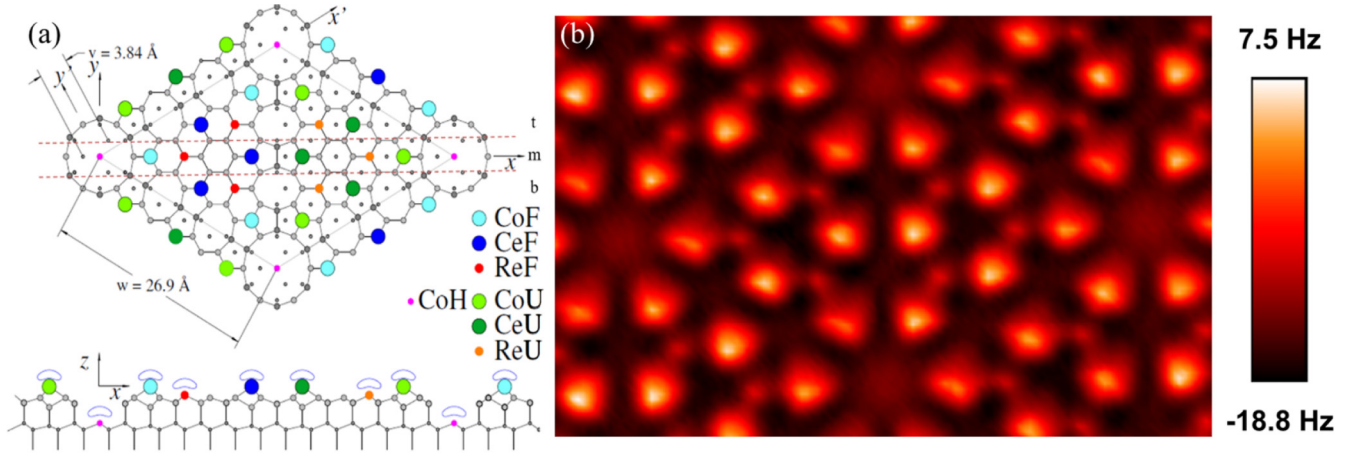


FIG. 1. (a) Top and side views of Si(111) 7×7 surface. The 12 adatoms fall into four classes: corner faulted (CoF), center faulted (CeF), corner unfaulted (CoU), and center unfaulted (CeU); the six rest atoms fall into two classes: rest faulted (ReF) and rest unfaulted (ReU). “t,” “m,” and “b” indicate the top half, the middle part, and the bottom half of the surface respectively. (b) Experimental constant height AFM image of the Si(111) 7×7 surface imaged with a CO terminated tip. Panel (a) is adapted from our previous work [15].

suggesting a bending of the CO tip. In our experiments, we employ a commercial low-temperature combined scanning tunneling/atomic force microscope operated at a temperature of 4.4 K (LT STM/AFM, Scienta Omicron GmbH, Taunusstein). The microscope utilizes a qPlus sensor type M4 (see Table I in Ref. [34]) to sense the tip-sample force and the tunneling current. We use a sensor with an etched W tip that is terminated with a CO molecule, showing a resonance frequency of $f_0 = 55\,056$ Hz, a stiffness of $k = 1850$ N/m, and a quality factor of $Q = 2\,053\,900$. The sensor is operated at a constant amplitude of $A = 50$ pm in the frequency modulation mode (FM-AFM) [33], with a phase-locked-loop bandwidth set to $B = 25$ Hz. In FM-AFM, the frequency shift Δf of the sensor from its unperturbed resonance frequency f_0 can be related to the gradient of the vertical force between tip and sample k_{ts} as $\Delta f = f_0 \langle k_{ts} \rangle / (2k)$, where the brackets indicate a weighted average over the oscillation amplitude of the tip [35]. Both the pure and B-doped Si samples are prepared by flash annealing to 1550 K for 15 s by direct current heating as provided by the Scienta Omicron sample holder. The sample is doped to a dopant density of $10^{19}/\text{cm}^3$, which corresponds to about one B atom per 5000 Si atoms. The pressure in the preparation chamber is kept below 5×10^{-7} Pa during the flash cycle to obtain a clean sample. We let the sample cool down to room temperature and transfer it to the low-temperature microscope. All AFM measurements were conducted at zero bias because flickering occurs at a small distance. Applying a bias would result in a large current and potentially cause the loss of the tip.

Here, we report an image flickering phenomenon for experimental measurements on heavily B-doped Si(111) 7×7 reconstructed surfaces. This phenomenon is manifested as an alternating brightening and dimming of Si adatoms' appearance in SPM images when the probe tip height is adjusted. It is observed when using AFM and STM to image the B-doped Si surface. For the AFM images, we only observed the flickering phenomenon on one of the CeF adatoms (movie clips 1 and 3), whereas in the STM images, this phenomenon occurred on every adatom (movie clips 2 and 4).

We employ pseudopotential-density functional theory (DFT) [36,37] calculations to understand and interpret the experimental findings. We introduce one single B dopant onto a Si(111) 7×7 surface consisting of 396 Si atoms and 49 passivated H atoms (see Supplemental Material Fig. 1 [38]). The H passivation method results in an electronically inert surface without altering the intrinsic properties of the surface [39,40]. We find that the B atom tends to reside in the surface layer, with the most favorable sites located directly underneath the 12 adatoms. This is likely because the B dopant tends to stay at or diffuse to the surface to minimize the strain and purify the interior [41]. Among these 12 sites, the most and least favorable sites exhibit an energy difference of ~ 0.1 eV and are positioned below the CoU_m and CeF_m adatoms, respectively. This implies that the entire system is likely to be heavily doped when the site underneath the CeF_m site is occupied by a B dopant. Our DFT calculations on the pure Si surface reveal that the heights of the four adatoms follow the order of sites CoF, CeF, CoU, CeU, which is consistent with previous calculations [11,12] and experiment [42–44]. We investigate the response of CeF_m and CeU_m sites (in both pure Si and 1B-doped systems) as a CO tip approaches. Despite the presence of a bistable structure on the Si surface [45], we find that only the CeF_m site of the B-doped system exhibits a sharp increase in the measured relative frequency shift (Δf), which is directly proportional to the AFM image's signal strength. Within this configuration, we posit that the observed flickering phenomenon of CeF sites, exclusively on the heavily B-doped Si surface in the AFM images, can be attributed to the presence of bistable structures and the pronounced responsiveness of CeF sites to the underlying B dopant.

We observe significant variations in the STM images of the heavily B-doped Si surface under positive and negative bias conditions. Specifically, when a negative bias is applied, many adatoms appear to vanish. We employ a simple system doped with one B atom to investigate the charging effect in STM experiments. We find the dangling bond of the adatom disappears from the simulated image in the presence of an

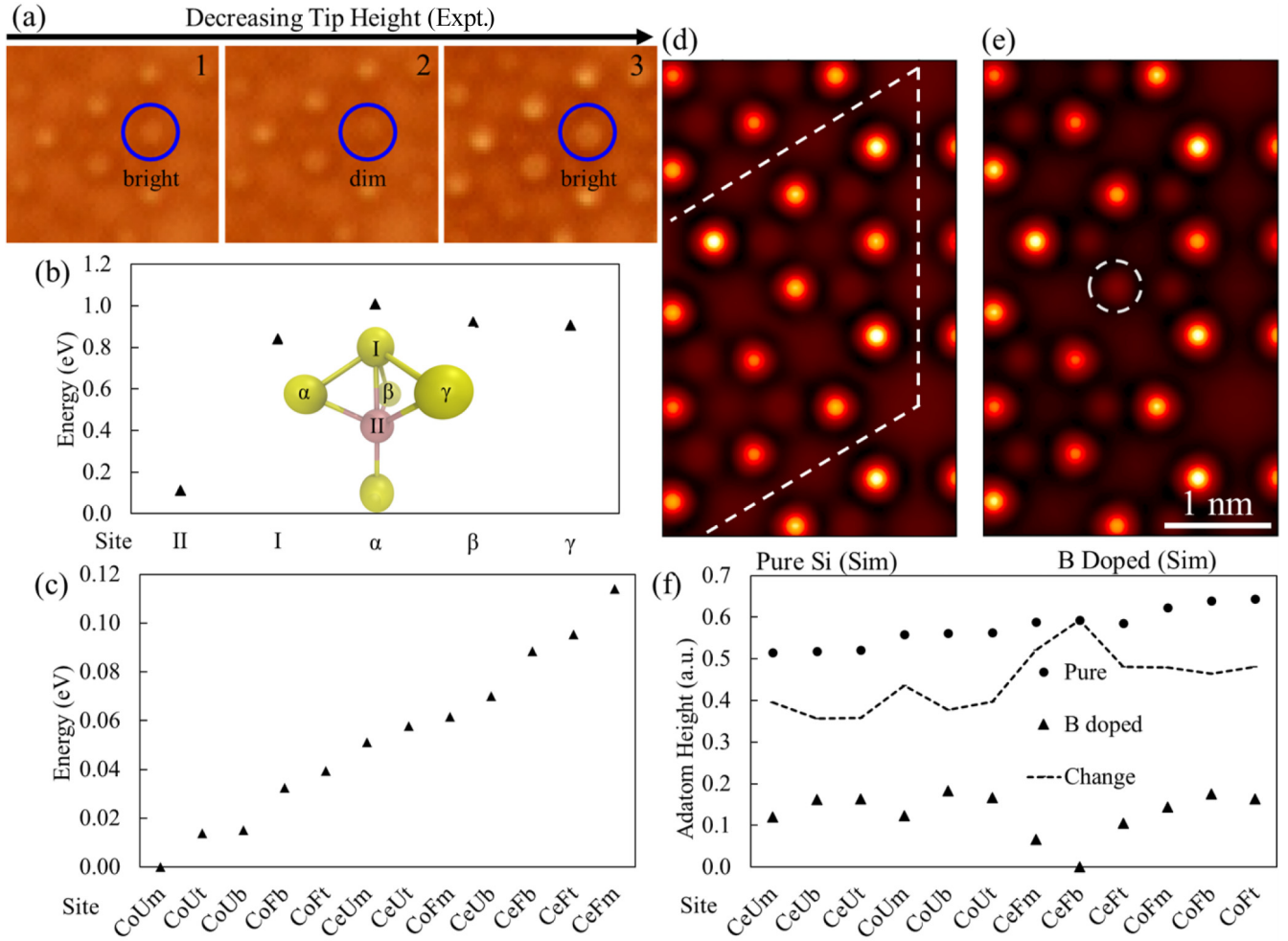


FIG. 2. (a) AFM images of a Si(111) 7×7 surface with decreasing tip height (from left to right). 1, 2, and 3 show the image flickering phenomenon on a CeF_m adatom. (b) Energetic favorable doping site determination around a CeF_m adatom (yellow: Si; pink: B). II is the underneath site; I is the CeF_m adatom site; α , β , γ are the three nearest Si neighbors; the unlabeled atom is in the first bulk layer, and the energy of zero corresponds to the doping of the underneath site of CoU_m site which has the lowest energy among all sites we test. (c) Energetic favorable doping site determination among all adatoms' underneath sites. [(d),(e)] Simulated AFM images of pure (d) and 1B-doped (e) Si(111) 7×7 surfaces. The diamond dashed box in (d) indicates a unit cell, the dashed circle in (e) indicates the location of the B dopant—underneath the CeF_m Si adatom. The tip height is 5.9 a.u. (f) Relative adatom heights for pure and B-doped systems. The atomic coordinate in the z direction (perpendicular to the surface) of CeF_b adatom is taken to be 0. The dashed line shows the change in adatom heights due to the B dopant underneath. Panel (a) is extracted from movie clip 1.

underlying B atom. If we introduce charges to the single B-doped surface, the first added electron goes to the adatom to regenerate a dangling bond, while the second electron is delocalized over the entire system. The regeneration of the dangling bond alters the density of surface states, which is directly proportional to the local differential conductance of the surface. As the tip height decreases, the perturbation exerted by the tip on the adatom causes continuous switching between the charged and neutral states of the adatom subunits. Consequently, the conductivity of the surface changes with the variation in tip height. This constitutes the origin of STM image flickering.

AFM imaging. Figure 2(a) displays the AFM images of the heavily doped Si surface captured at three different tip heights: 1, 2, and 3, in decreasing order from left to right (extracted from movie clip 1; see the Supplemental Material [38]). We note that the CeF_m adatom site within the blue circle initially

dims (from 1 to 2), but then brightens again (from 2 to 3). To confirm the preferred location of the B dopant, we compared the general trends when adding one B atom to the bulk layer and to the surface layer by employing a real-space pseudopotential code constructed within DFT-PARSEC [46–50] to perform total electronic energy and structural relaxation calculations (see the Supplemental Material for computational details [38]). We find that the surface layer site is energetically favorable compared to all the tested bulk layer sites. On average, the surface site is 1.1 eV more favorable than the bulk layer sites, with a standard deviation of 0.4 eV. The specific sites we selected and their corresponding total energies are provided in Supplemental Material Figs. 1 and 2 [38].

Given the preference of the B dopant to reside on the surface layer, we initially examine five sites surrounding the CeF_m adatom. As illustrated in Fig. 2(b), we find that the II site exhibits much greater favorability to be replaced by a

B atom, approximately 0.80 eV lower in energy compared to the other four sites (I, α , β , and γ). In a pure Si(111) 7×7 surface, the adatoms possess sp^3 hybridization, with each adatom featuring a dangling bond state perpendicular to the surface [4]. When a B dopant replaces the underlying Si atom, a hole state is formed, which accepts a single electron from the adatom. The formation of a Si-B bond between the B dopant and the adatom leads to full coordination of the adatom and thus stabilizes the system. We assume that sites around other adatoms behave in a similar fashion.

We evaluate the II sites for the remaining adatoms. Figure 2(c) presents the B preference across all adatoms. The CoU sites exhibit the highest favorability, while the least favorable sites are the CeF sites, where AFM image flickering occurs. We also examine the six rest atom sites. On average, the ReU and ReF sites are 0.55 and 0.73 eV less stable than the II site of the CoU_m adatom. We simulate the AFM images at a tip height of 5.9 a.u. for both pure [Fig. 2(d)] and 1B-doped [Fig. 2(e)] Si(111) 7×7 surfaces where the B atom is below the CeF_m Si adatom (see the Supplemental Material for details of AFM simulation [38]). By comparing Figs. 2(d) and 2(e), we confirm that the doped B atom causes a dimming effect on the AFM image of specific adatoms. The dashed circle in Fig. 2(e) indicates the location of the B dopant. Figure 2(f) shows the corresponding adatom heights for both the pure and B-doped systems, along with the associated height changes. We take the CeF_b (B-doped) adatom's height (relaxed) as a zero reference since it has the smallest height. For pure Si, the average heights of the adatoms (top, middle, and bottom) within the same group are as follows: CoF (0.636 a.u.) > CeF (0.589 a.u.) > CoU (0.561 a.u.) > CeU (0.5187 a.u.). This is further confirmed by the electron density profiles above the surface (see Supplemental Material Fig. 3 [38]). The heights within one group are very close (less than 0.02 a.u. difference). Our calculation gives the same trend as previous studies [11,12,27,42,43]. For one B-doped system, the average adatom heights are CoF (0.161 a.u.) > CoU (0.157 a.u.) > CeU (0.148 a.u.) > CeF (0.057 a.u.). We find that the presence of a B dopant beneath the CeF_m adatom indicates a heavily doped system. This is due to the fact that the II site of CeF_m is the least favorable one among the 12 adatom II sites [Fig. 2(c)] and explains why we can only observe flickering phenomena at the CeF_m site in the AFM images of heavily B-doped systems.

However, although the dashed line in Fig. 2(f) illustrates that CeF sites exhibit the most pronounced response to the introduction of B dopants, this alone does not fully explain why this response leads to AFM image flickering. We further investigate the interaction between the CO tip and the B-doped Si subunit theoretically. We gradually reduce the tip height above a Si adatom with a B dopant underneath and perform structural relaxation by allowing all surface atoms (top two layers) to move freely at each height. As shown in Fig. 3(a), as the tip approaches the surface (decreasing Δz), the adatom subunit undergoes a process of compression followed by elevation, with $d_{\text{Si-B}}$ decreasing and then increasing to a value greater than when there is no tip present. This structural modulation indicates the presence of a bistable structure.

We then examine the modulation behavior by comparing the calculated vertical forces, F_z [Fig. 3(b)], the relative adatom heights [Fig. 3(c)], and Δf [Fig. 3(d)] of a 1 B-doped system and a pure Si system at both the CeF_m and CeU_m sites. From the force curves in Fig. 3(b), we observe that the formation of a bistable structure of the adatom subunit is an inherent property of the Si(111) 7×7 reconstruction surface, independent of whether the system is B-doped or not and whether it is located on the faulted or unfaulted side. By comparing the two solid lines and the two dashed lines in Fig. 3(c), we find that regardless of the presence of a B dopant, the physical oscillation of the adatom on the CeF side is always stronger than on the CeU side. Surprisingly, for small tip heights (~ 3.5 a.u.), the popping phenomenon is more pronounced in pure Si compared to B-doped Si, yet we only observe the flickering phenomenon in AFM images on the B-doped surface. As a result, we compute Δf as a function of Δz [Fig. 3(d)] and find that the Δf spectrum for both CeF and CeU adatoms is much more similar for the pure system compared to the spectrum for the B-doped system. As indicated by the green arrows in Fig. 3(d), for the B-doped system, there is a sudden jump for the CeF_m adatom when Δz is approximately 3.5 a.u., while the CeU_m adatom is at its minimum. This explains why we only observe AFM image flickering in the B-doped system. Our calculations demonstrate that this flickering phenomenon arises directly from the interaction between the CO-terminated tip and the B-doped Si subunit. The tip is not merely a measurement tool here, but an integral part of the system [51], influencing the surface structure.

To further substantiate our findings, we compared the experimentally measured Δf and F_z , for three systems: the undoped Si surface (Supplemental Material Fig. 8 [38]) and two heavily B-doped Si surfaces (Supplemental Material Figs. 9 and 10 [38]). Our experimental results confirm that the AFM image flickering phenomenon indeed occurs at the CeF_m sites in the B-doped systems, supporting our theoretical predictions. Our results provide a viable explanation for the occurrence of flickering in the AFM image of the CeF_m site in heavily B-doped Si surfaces.

STM imaging. Similar to AFM imaging, we observe image flickering in the STM images of the heavily doped Si(111) 7×7 surface as the tip height decreases [Fig. 4(a)], extracted from movie clip 2; see the Supplemental Material [38]). Unlike AFM experiments, which are highly sensitive to imaging height as they measure quantum forces, STM images typically only vary with changes in the applied bias voltage as long as it is near the set point. In experiment, we investigate the empty [Fig. 4(b)] and filled [Fig. 4(c)] states by applying bias voltages of +600 and -500 mV, respectively (see Supplemental Material Fig. 4 [38] for large-scale topographic STM images). In our simulation, to meet the requirements of the heavily doped system, we first investigate a 12 B-doped system with each adatom's II site hosting a B dopant. We calculate the empty [Fig. 4(d)] and filled states [Fig. 4(e)] for this system near the Fermi level, at +0.55 eV and -0.41 eV, respectively. Our calculations reveal that when a positive applied bias is used, each adatom exhibits a bright spot appearance [red spots in Fig. 4(d)]. On the contrary, Fig. 4(e) shows that some adatoms seem to disappear or exhibit much weaker signals,

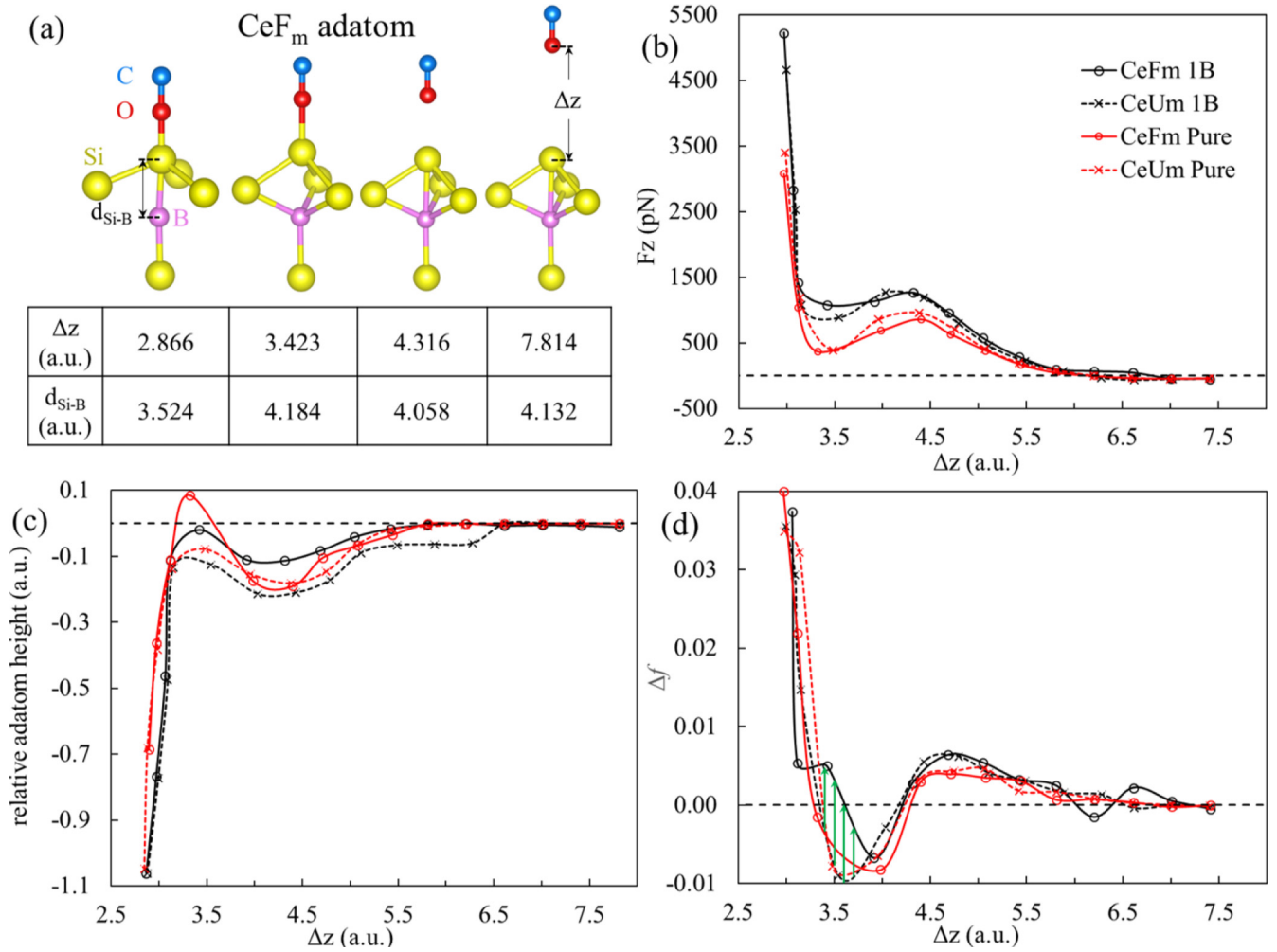


FIG. 3. (a) Optimized structures of the B-doped Si subunit at the CeF_m site as the CO tip approaches the adatom. Δz and $d_{\text{Si-B}}$ denote the tip-adatom distance and the distance between the adatom and the underlying B dopant. [(b)–(d)] Calculated properties at CeF_m (solid lines) and CeUm (dashed lines) sites, with black and red representing 1B-doped and pure Si systems, respectively. (b) Vertical forces (in pN) acting on the tip; (c) relative adatom height (in a.u.), with zeros corresponding to the height of the adatom when the CO tip is absent; (d) relative frequency shift Δf , which is directly proportional to the signal strength at the corresponding site on AFM images. The green arrows highlight the Δf variation at the CeF_m and CeUm sites when the tip height is in the range of 3.4–3.7 a.u.

especially on the unfaulted side, while some rest atoms become visible when applying a negative bias. The signals from the rest atoms are stronger than those from the adatoms in the simulated image [Fig. 4(e)], which does not perfectly match our experimental image [Fig. 4(d)]. This discrepancy arises from the inherent randomness in the distribution of B dopants during the annealing process, which we cannot precisely control in experiments. Our simulation here only illustrates one scenario where each adatom has a B dopant underneath. We find the rest atoms vanish from the negative bias image when they are also replaced by B dopants (see Supplemental Material Fig. 5 [38]). Furthermore, we observe that in most of the unit cells shown in the large topographic image (negative bias), the visible CeF adatoms are much more numerous than the CeU adatoms. This is consistent with our simulation which tests the scenario where the B atoms are evenly distributed on both sides.

To accurately investigate the process of surface charging, we simplified our system by employing a 1-B-doped system.

Figures 4(f)–4(i) show the charge density of selected wave functions on a plane above the surface for both pure and B-doped Si (II site of CeF_m adatom) for the empty states with a biased voltage of +0.60 eV (see Supplemental Material Fig. 6 [38] for the corresponding filled states images). All the volume slices are taken at the same height. The B dopant underneath leads to a missing state above the adatom. This supports our previous conclusion that the Si adatom becomes fully coordinated when there is a B dopant underneath, which results in the dangling bond disappearing. The dangling bonds of the adatoms are believed to be directly related to the high conductivity of the $\text{Si}(111) 7 \times 7$ surface [12]. The disappearance of the dangling bonds leads to a decrease in the conductivity of the surface. The conductivity of the sample has a direct impact on the STM image. A study on heavily B-doped $\text{Si}(111) \sqrt{3} \times \sqrt{3}$ surface shows that the Si subunit can be charged, and the charged state exhibits an elevated geometry [45]. We investigate the -1 and -2 charged B-doped $\text{Si}(111) 7 \times 7$ surfaces and observe a similar trend.

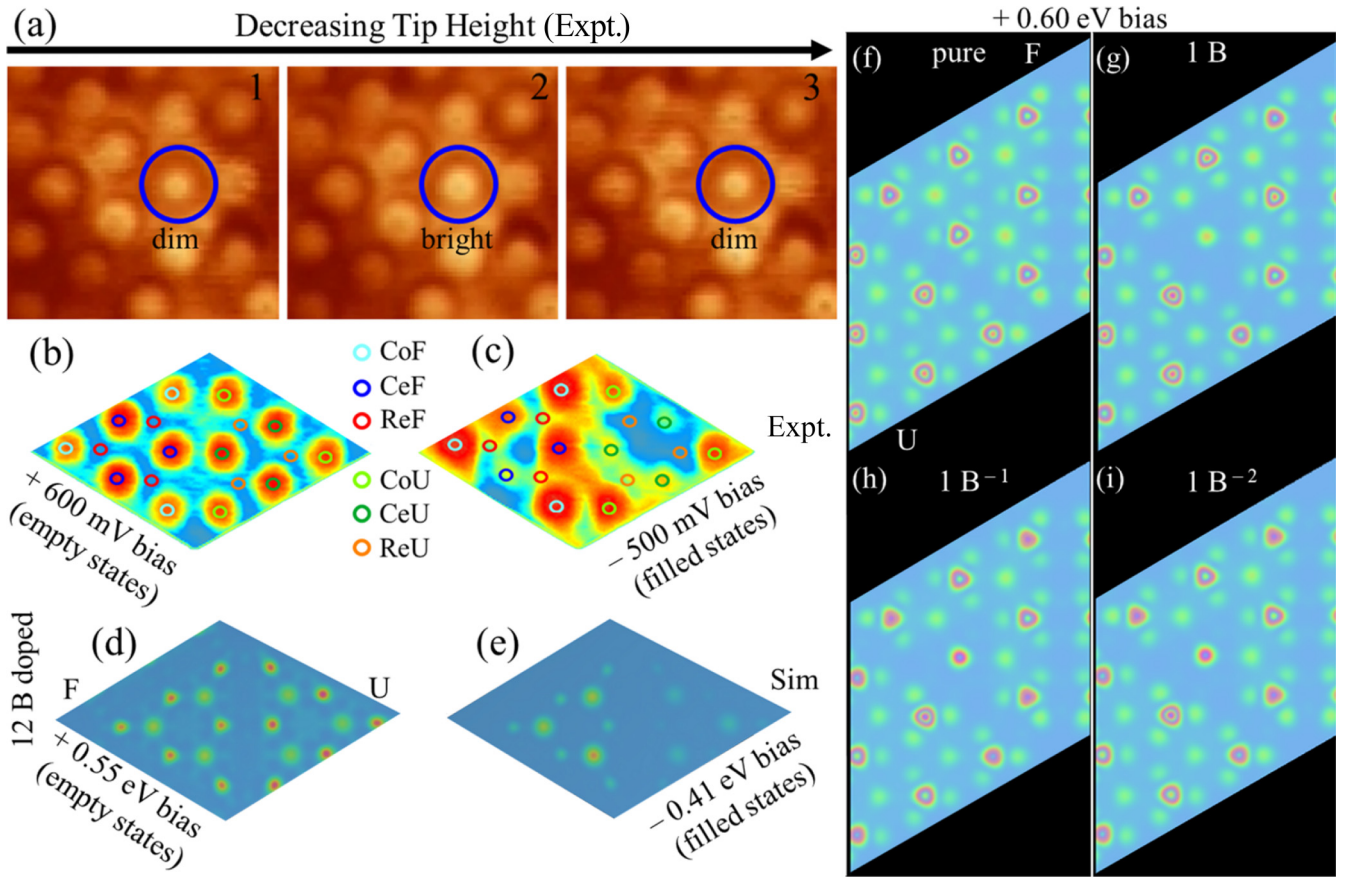


FIG. 4. (a) STM images of a Si(111) 7×7 surface with decreasing tip height (from left to right). 1, 2, and 3 show the image flickering phenomenon on a CeF_m adatom. [(b),(c)] Experimental STM images of a Si(111) surface with different applied bias. (b) +600 mV, (c) -500 mV. The current setpoint is 10 pA. [(d),(e)] DFT calculated (d) empty states (+0.55 eV) and (e) filled states (-0.41 eV) of a 12 B-doped system where the II site of each adatom is occupied by a B atom. [(f)–(i)] The square of the absolute value of the selected empty state (0.60 eV above the Fermi level) wave functions on a plane above the surface. The B dopant is underneath the CeF_m adatom. (f) Pure Si surface; (g) B-doped surface (net charge = 0); (h) B-doped surface (one electron added); (i) B-doped surface (two electrons added). For pure Si surface (f), the plane is 0.5 a.u. above the CeF_m adatom; for B-doped surface (g)–(i), the plane is 1.0 a.u. above the CeF_m adatom. Red-green-blue scale is used (red is for higher density). The labels *F* and *U* in (d) and (f) indicate the faulted and unfaulted sides, respectively. Panel (a) is extracted from movie clip 2.

Figures 4(g) and 4(h) show that when one electron is added to the system, it goes to the CeF_m adatom site as the dangling bond state occurs again. Figures 4(h) and 4(i) show that when the second electron is added to the system, it is delocalized over the system. Volume slices along the *z* direction, which is perpendicular to the planes in Fig. 4, show a clear formation of the dangling bond and the delocalization of the second added electron (Supplemental Material Fig. 7 [38]). The conductivity of the surface constantly changes during STM experiments owing to the switchable states and the movement of the tip.

In conclusion, we employ a combined theoretical and experimental approach to investigate the image flickering phenomenon observed in AFM and STM experiments on heavily B-doped Si(111) 7×7 surfaces. In AFM images, we only observe this phenomenon at the CeF sites in heavily B-doped systems. There are two main reasons for this. On the one hand, the II site near the CeF adatom is the least energetically favorable doping site compared to the II sites around other adatoms, implying that this site is more likely to be replaced by B in a heavily doped system. On the other hand, compared to the CeU site, the B-doped CeF site shows a significant relative

jump in the measured Δf when the tip height is between 3.4 and 3.7 a.u. as Fig. 3(d) shows. In STM images, the adatoms can regenerate the dangling bonds lost in the presence of B when they accept electrons. STM image flickering arises due to the charge/discharge behavior of the B-doped subunit under the influence of the biased voltage and the perturbations introduced by the tip.

The discovery of substantial alterations in the properties of a Si(111) 7×7 surface upon B doping holds profound implications across various fields. The intriguing impact of dopants on the structural stability of the Si lattice adds depth to this research. In a previous investigation [52] into DX center formation in GaAs and Al_xGa_{1-x}As alloys, the intricate interplay between dopants and lattice structures becomes apparent. The study on DX centers elucidated that strain-induced lattice distortions play a pivotal role as significant contributors to energy shifts in electronic states.

Considering silicon's central importance in semiconductor technologies, comprehending how dopants influence electronic structure offers novel approaches to the development of electronic devices and quantum technology development. The

distinctive insights gained from our study contribute to the evolving landscape of semiconductor physics and materials science, shedding light on the intricate relationship between dopants and the structural stability of Si-based systems.

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