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Characteristic adsorption of Xe on a Si(111)-(7×7) surface at low temperature

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Site-dependent adsorption structures of Xe atoms on a Si(111)-7×7 surface were studied by scanning tunneling microscopy at 8 K. Xe atoms initially adsorb as dimers on the site between a rest atom and its two neighboring center adatoms, and then near the corner adatom site. Similar structures were formed at both the faulted half (FH) and the unfaulted half (UH) of the 7×7 unit. The observed structure is in excellent agreement with that estimated by the rigid ball model, however, site-dependent bias dependence and different stabilities were observed for them, indicating the existence of different interactions between Xe and Si atoms in the 7×7 unit despite the stable electronic structure of Xe. Based on the results with thermal desorption spectroscopy, the adsorption energies are estimated to be 200 and 220 meV for FH and UH units, respectively.

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The interaction among rare-gas atoms on various surfaces has been widely studied to understand the characteristics of ideal gas systems since they have simple and stable electronic structures.^{1,2} Recently, scanning tunneling microscopy (STM) studies have revealed intriguing phenomena.³⁻⁶ For example, Xe atoms on Pt(111) and Cu(111) surfaces exhibit completely different behaviors at step edges.³⁻⁵ Xe atoms on the Pt(111) surface are preferentially adsorbed at the upper step edges, while Xe atoms on the Cu(111) surface are preferentially adsorbed at the lower step edges and form one-dimensional chains. The following growth processes of them are completely different from each other. The measurement of the change in the dispersion of the Cu surface state with Xe adsorption is a good example to demonstrate the complex nature of Xe adsorption.⁷ These phenomena indicate the existence of the complicated interaction between rare gases and substrate metal surfaces despite the stable structure of the rare gases. Namely, the adsorption of rare gases modifies the substrate electronic structures, and the subsequent rare gases can probe the change in the electronic structure, resulting in the complicated adsorption processes.

In order to understand the interesting and important rare-gas behavior comprehensively, understanding of Xe growth mode on the surface with well-defined electronic structure is essential. In this paper, we report the adsorption processes of Xe on a Si(111)-7×7 surface by STM at 8 K. The Si(111)-7×7 surface has been used as a model surface to understand chemical reactions, because it consists of several atoms with well-defined electronic structures: namely, corner, center, and rest atoms in faulted half (FH) and unfaulted half (UH) units. Therefore, characteristic features of the Xe adsorption process can be analyzed directly. We report unusually complex adsorption structures on Si(111)-7×7.

As-doped, *n*-type Si(111) samples with a conductivity of 0.37–0.625 Ωcm were flash-cleaned at ~1500 K for 30 sec, and then annealed at ~1100 K for 30 sec before cooling. The base pressure was 7×10^{-9} Pa, and was remained below 2×10^{-8} Pa during the cleaning process. After a completed 7×7 structure was obtained, the samples were cooled to 8

K. Xe dosing was performed using an electronically controlled pulse valve. An electrochemically etched tungsten tip, was retracted from the sample during the Xe gas exposure, and STM imaging was performed over the area. The sample temperature was monitored using an Au+0.07% Fe-Cr thermocouple located near the sample.

Figure 1 shows a typical structure of adsorbed Xe atoms observed at various locations on the same surface. Xe atoms were not stable during STM measurement, but site-dependent structures were clearly visible. As shown in Figs. 1(a)–1(c), in the FH unit at low coverage area, adsorbed Xe atoms were imaged as elliptical bumps and three types of adsorption structures were distinguished, as named (a) 1D, (b) 2D, and (c) 3D structures, respectively. Figure 2(a) shows a magnified image of an elliptical bump, and the cross section along *A-B* in Fig. 2(a) is shown in Fig. 2(c). There exist two small peaks in the graph. Since the separation is close to the value of the Xe diameter, 4.3 nm, we consider that the elliptical bump is a Xe dimer.

At the high coverage area, three additional types of adsorption structures were observed, as shown in Fig. 1(d); namely, 3D+1C, 3D+2C, and 3D+3C structures. Here, *C* means the additional bump observed near the corner adatom sites. Those bumps were not stable, and when they moved during STM scanning, white-stripe noises were imaged, as indicated in Fig. 1(d) by the red arrows. The each of those bumps is considered to be a Xe atom adsorbed on the Xe dimer and corner adatom. In fact, when the corner Xe atom moves away under STM scanning, a Xe dimer in the first layer appears. For comparison, some of the structures are schematically depicted in Fig. 1(e). Green and yellow circles indicate the Xe dimer and corner atoms, respectively.

As is evident in Fig. 1(d), similar structures are observed in the UH unit, which consists of corner Xe adatoms on the 3D structure. The Xe dimer structures without the upper corner Xe atoms were, however, not observed in the UH unit even with low Xe coverage, and only the 3D+1C, 3D+2C, and 3D+3C structures were observed stably. For example, 3D+2C and 3D+3C structures are shown in Fig.

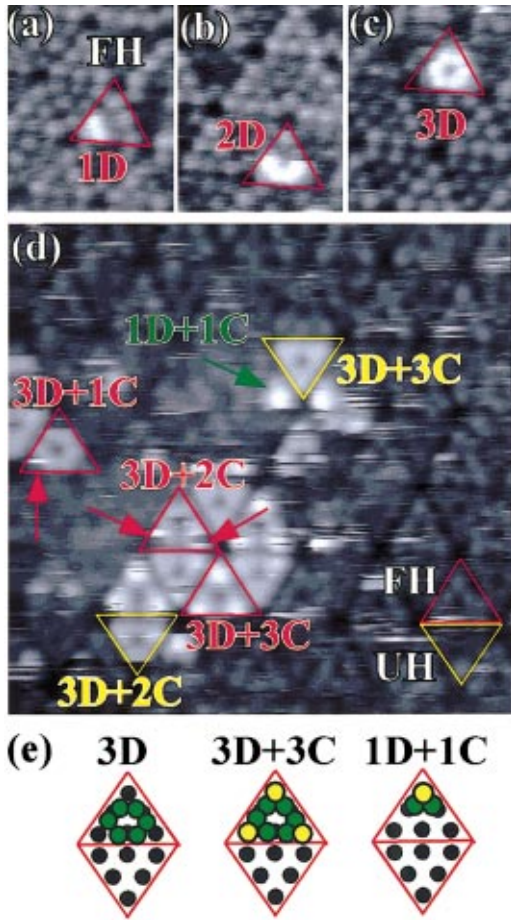


FIG. 1. (Color) (a)–(d) Structures of Xe atoms adsorbed on Si(111)- 7×7 surface at 8 K ($V_s = -2$ V, $I_t = 0.3$ nA). (e) Schematic models of 3D, 3D+3C, and 1D+1C.

1(d), as indicated by yellow triangles. Figure 2(b) shows a magnified STM image of 3D+2C structures in the UH units. The cross section along C-D in Fig. 2(b) is similar to that of A-B as shown in Fig. 2(c), indicating the existence of the dimer structure in the case of the UH unit, too. Although the structures described above represent the majority, trimer structures that consist of 1D+1C [Fig. 1(e)] were observed in some FH units, when the neighboring UH unit is occupied by Xe atoms. An example is shown in Fig. 1(d) as indicated by the green arrow.

It must be pointed out that our STM images were obtained on Xe adsorbed surface and Xe atoms are mobile during the STM scan. Therefore, the actual growth process was not observed in real time. However, the adsorption process can be derived from the observed structures as follows: (1) Xe atoms are adsorbed in a dimer structure, resulting in the hexagonal shape formed by three dimers, as shown in Fig. 1(c) [green circles in Fig. 1(e)]. (2) After formation of the hexagonal structure consisting of three Xe dimers, Xe atoms are adsorbed one by one on the three corner sites contacting the Xe dimers [yellow circles in Fig. 1(e)]. Some information, such as whether UH or FH units are occupied by Xe atoms first, could not be obtained from our results, due to the mobility of Xe during the STM scan.

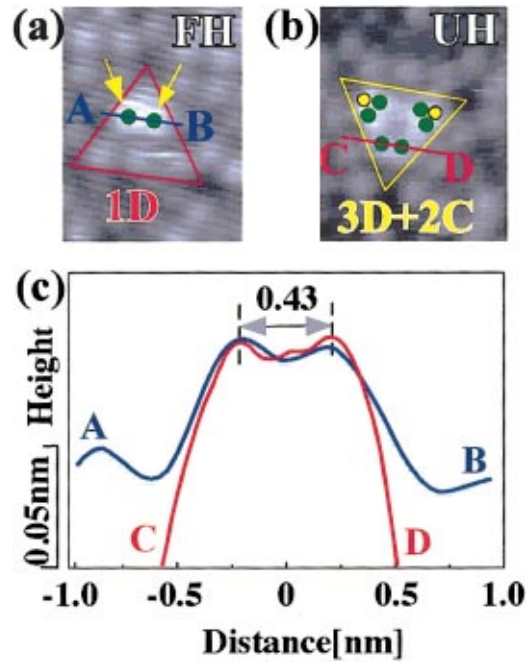


FIG. 2. (Color) Magnified STM images of (a) 1D' in FH and (b) 3D+2C in UH ($V_s = -2$ V, $I_t = 0.3$ nA). (c) Cross sections along A-B in (a) and C-D in (b).

With further exposure, the 3D+3C structure covered the entire Si(111)- 7×7 surface. Based on analysis of the cross sections, this structure was confirmed to consist of only a single adsorption layer of the 3D+3C structure. No further adsorption of Xe atoms on the complete adsorption layer was observed in our measurement, which may be due to the instability of the structure under STM measurement.

In order to confirm the present structural model we adopt a very simple rigid ball model with the atomic radii of Xe and Si atoms to be 0.217 and 0.117 nm, respectively, and the Xe atoms are assumed to be located at high coordination sites. When two Xe atoms were located at the positions indicated by the red arrows in Fig. 3(a), contacting the blue colored Si atoms, a rest atom, its neighboring center adatoms, and one of the Si atoms to which the center adatom is bonded, the distance between the two Xe atoms became approximately 0.43 nm, which is almost equal to the diameter of the Xe atom. Subsequently, each of the corner Xe atoms was placed in contact with a corner Si atom and a Xe dimer adsorbed in its neighboring site. The positions of the Xe atoms in our model are summarized in Fig. 3(b). The heights of the Xe atom positions are measured from the top of the corner adatom in the FH unit. In the UH unit, the values measured from the corner adatom in the UH unit are shown together in the brackets. Note that the atomic structure in the FH and UH units are almost the same, reflecting the fact that the first two Si layers of DAS model have almost the same in both half units.⁸

Figure 3(c) shows the cross sections obtained along the longer diagonal of the 7×7 unit with and without adsorbed Xe atoms. The thermal drift was corrected before the cross-section analysis. The red and black cross sections are obtained for the 3D+3C and bare 7×7 structures, respec-

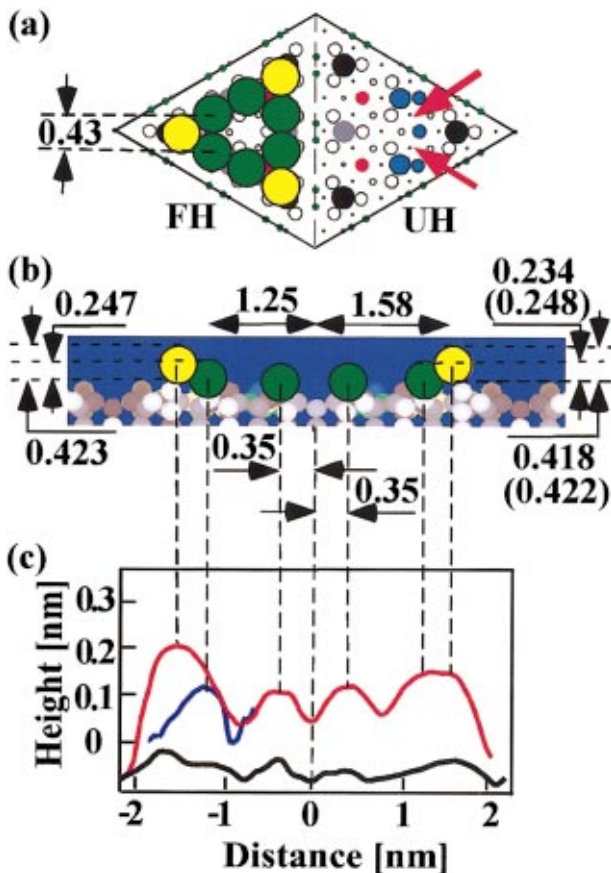


FIG. 3. (Color) (a) Adsorption sites used for calculation. (b) Calculated structures of the adsorbed Xe with the assumption of the rigid ball model. (c) Cross sections experimentally obtained along the longer diagonal of the 7×7 structure.

tively. The blue cross section in the FH unit was measured on a 3D structure without upper Xe atoms. Numerous cross sections were examined. The position of the corner hole was determined from the threefold rotational symmetry of the surface structure to compare the peak position with the calculated atom positions, which are indicated by arrows with the distance from the half unit boundary. It is evident that the observed peak positions in the cross sections are in excellent agreement with our structural model that employs simple assumptions. As is well known, the STM peak position does not always correspond to the actual atom position. In the present system, however, the Xe has a closed shell structure and the interaction of rare-gas atoms with neighboring atoms can be expected to be so small as to modify it negligibly. Thus, we consider the agreement seen here to be strong evidence of the validity of our structural model.

One must consider why Xe atoms adsorb in this specific manner, although many other high coordination sites exist in Si(111)- 7×7 units. Unless the Xe atoms prefer to form dimers initially and those in the second layer prefer to be adsorbed on corner adatoms, many other configurations can be imagined. Thus, the adsorption process must be a sign of the characteristic interaction between Xe and Si. In the case of C_{60} on Si(111)- 7×7 ,⁹ single molecules are also adsorbed at the high coordination sites, in agreement with weak and

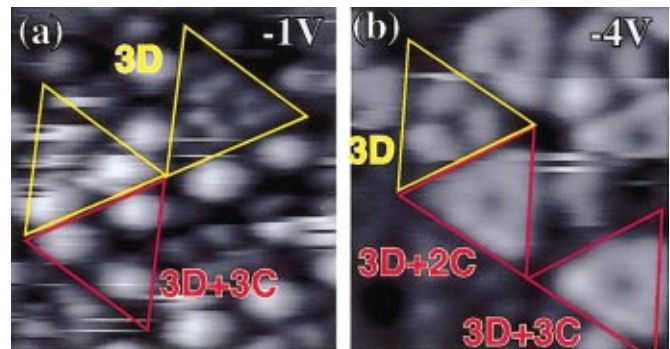


FIG. 4. (Color) STM images taken at $V_s = -1$ and -4 V ($I_t = 0.3$ nA).

noncovalent or chemical bonding between C_{60} and Si. Instead, small amount of charge transfer from Si to C_{60} is believed to exist. That results in a weak electrostatic bonding and produces the site preference. The site immediately above rest atom, which has the highest electron density, is the most preferential sites as expected, but the corner hole site and the sites on the dimer chain are also occupied with C_{60} with less probability. On the other hand, in the case of Xe, the preferential sites are located between a rest atom and its neighboring center adatom with much higher selectivity. Center adatoms are the sites with less electronic density.

In the 7×7 units, charge transfer takes place from adatoms to rest atoms, and there exist induced dipolelike electronic structures between atoms in a unit. Since center adatoms are less charged compared to corner adatoms, a stronger dipole between rest atoms and center adatoms may interact with Xe atoms. The positions determined by the calculation are the high coordination sites for the formation of Xe dimers. Once a Xe dimer is formed, the sites between the Xe dimer and its neighboring corner adatom also become high coordination sites for Xe, and the dipole between a corner adatom and a neighboring rest atom may be attractive for the subsequent Xe atoms. As observed in the cases of Xe adsorption on metal surfaces, Xe atoms adsorbed at the step edges induced repulsive interaction with the subsequent Xe atoms.³⁻⁵ However, since no single Xe atom was observed in this case, the dimerization of Xe atoms is necessary for the stability of the first layer structure. In order to explain the adsorption structure, it is necessary to understand the electronic structure of the adsorbed Xe atoms. An excellent agreement was obtained for the model and experimental results regarding the lateral positions of Xe atoms; however, as shown in Fig. 3, the apparent heights of the Xe atoms do not coincide with that obtained with our structural model. In addition, although the final structures are the same in FH and UH units, Xe atoms at the different sites showed different stability under STM scan, indicating the difference in the stability of the structures with different electronic structures.

The difference and similarity between the electronic structures of Xe atoms at different sites were confirmed at various bias voltages. STM images taken at -1.0 and -4 V are shown in Fig. 4. At -1.0 V, in comparison to the image at -2 V, Xe dimers become darker and, in contrast, the apparent height of the corner Xe atoms was emphasized. Further-

more, in the dimer structure, the central part is particularly dark, and its two Xe atoms are clearly separated, as shown in Fig. 4(a). The observed change was similar in both units. On the other hand, at -4 V, the central part of the dimers becomes brighter, and the dimers appear to have a beanlike shape. According to a local density approximation calculation, a hybrid electronic structure is formed between the Xe atom and the substrate. In the case of a metal substrate, hybrid state is formed near the Fermi level. The observed bias dependence at higher voltage is considered to be due to the position of the Si surface states. This local density of state observed at the center of a dimer in the deep filled state might be an indication of the bonding state between the two Xe atoms.

In addition, the three dimers in the FH unit are more separately imaged from each other than those in the UH unit, indicating that the interaction reflects the difference in the electronic structure between FH and UH units. As shown in this paper, the growth model has several steps, indicating the existence of corresponding stable structures in the processes. In fact, based on the comparison of STM images, the first and second layers show different site-dependent electronic structures.

In the previous thermal desorption spectroscopy (TDS) measurement of Xe/Si(111)- 7×7 , several different adsorption states with different desorption energies were observed, five peaks at ~ 67 K (*D*), ~ 80 K (*C'*), ~ 87 K (*C*), ~ 93 K (*B*), and ~ 97 K (*A*).¹⁰ The peak at ~ 67 K (*D*) with the lowest energy was attributed to the multilayer adsorbates. The ratio of the two major peaks at ~ 80 K (*C'*) and ~ 87 K (*C*) was 1:1 and the amount of the other two peaks was much smaller. There are four different types of Xe atoms in our structural models, which are Xe dimer and corner atoms in both FH and UH units. The atom numbers are 3:6:3:6 for [UH corner]: [UH dimer]: [FH corner]: [FH dimer]. Thus, the only possible assignment is to attribute the entire $3C+3D$ structure in FH and UH units to the two major peaks of (*C'*) and (*C*). The difference in the first and second layer in each

half unit is assumed to be unresolved. Since UH units are more stable under STM measurement, the structure in the UH unit is assigned to the higher temperature peak. The remaining two peaks of (*B*) and (*A*) may be from the defect- or step-related adsorption sites. In consideration of these findings, the binding energies of Xe atoms in FH and UH units are estimated to be 200 and 220 meV, respectively.

The obtained site-dependent bias dependence in STM images directly indicates the existence of the interaction between Xe atoms and the Si substrate. This interaction changes not only the electronic structure of Xe, but also that of the substrate, although the change in the electronic structure of the substrate could not be observed in the STM images. The change in the electronic structure of the substrate is probed by the Xe adsorption process itself. In fact, as shown in Fig. 1(d), the unit cells with the Xe atoms exhibit a tendency to cluster, which suggests the existence of an indirect interaction between adsorbed Xe atoms through modulation in the Si substrate electronic structure. Note that Xe atoms in neighboring half units are too far apart to interact directly. In addition, as mentioned previously, the $1D+1C$ structure formed in UH units was observed only when Xe atoms were present in the neighboring FH units. Although further theoretical study is needed, the observed interaction between the rare gases and the substrate is considered to play an important role in the characteristic interactions of rare gases adsorbed on the transient metals.

In conclusion, site-dependent adsorption of Xe atoms on a Si(111)- 7×7 surface were studied by STM at 8 K. The adsorption sites were in excellent agreement with those calculated by the rigid ball model. However, from the analysis of the bias dependence, the site-dependent interaction between Xe atoms and the Si substrate was confirmed. The existence of the indirect long-range interaction between the rare-gas atoms through the modulation of the substrate was also observed. This is an observation of the interaction between Xe atoms and the substrate with well-defined electronic structure at the atomic scale.

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