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# Correlation between Adatom-Adatom Pair Interaction and Adlayer Superstructure Formation: Si on W{110}

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Pair energies for Si adatoms on the W{110} for several bond lengths were obtained by direct field-ion–microscopy observations. Maximum binding occurred at a distance $\sqrt{2}a$ in the $[1\bar{1}0]$ and maximum antibinding at $a$ in the [001]; $a$ is the lattice constant. From the data, the two-dimensional binding energy per adatom in an adlayer can be calculated. The $[2\sqrt{2}/\sqrt{3} \times 4/\sqrt{3}\,]R35.26°$ superstructure has the lowest energy. Our search for a superstructure formation by thermal equilibration of Si adatoms confirmed this prediction.

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Low-energy–electron-diffraction (LEED) experiments have revealed that when a chemically reactive gas chemisorbs on a clean surface, the adlayer very often forms a superstructure.[1] Somorjai and Szalkowski,[2] and perhaps some others, believed that adatom-adatom interaction was responsible for the superstructure formation. Einstein and Schrieffer[3] proposed that the superstructure formation was due to the oscillatory nature of an "indirect" adatom-adatom interaction.[3-6] This theory, although it has been around for some years, still lacks direct experimental evidence. Field-ion–microscope (FIM) studies of adatom-adatom interactions with use of metal

TABLE I. Bonds observed out of 515 heating periods at 300 °K. Configurations refer to Figs. 1 and 2.

| Configurations | Bond directions | Bond lengths | Frequencies of observation | Statistical weights | Relative binding energies |
|---|---|---|---|---|---|
| *a* | $\sim[1\bar{1}1]$ | $\sim 2.74 \pm 0.30$ Å, or $\sim(\sqrt{3}/2)a$ | 28 | ~4 | 0 (reference level) |
| *b* | [001] | $3.16 \pm 0.30$ Å, or $\sim a$ | 3 | ~2 | $-40 \pm 12$ meV |
| *c* | $[1\bar{1}0]$ | $4.47 \pm 0.30$ Å, or $\sim(\sqrt{2})a$ | 82 | ~2 | $46 \pm 2$ meV |
| *d* | $[1\bar{1}1]$ | $5.48 \pm 0.30$ Å, or $\sim(\sqrt{3})a$ | 14 | ~4 | $-18 \pm 6$ meV |
| *e* | [001] | $6.32 \pm 0.30$ Å, or $\sim 2a$ | 9 | ~2 | $-11 \pm 7$ meV |
| *f* | $[1\bar{1}0]$ | Two $4.47 \pm 0.30$ Å bonds | 4 | ... | ... |
| *g* | $[1\bar{1}0]$ | Three $4.47 \pm 0.30$ Å bonds | 1 | ... | ... |

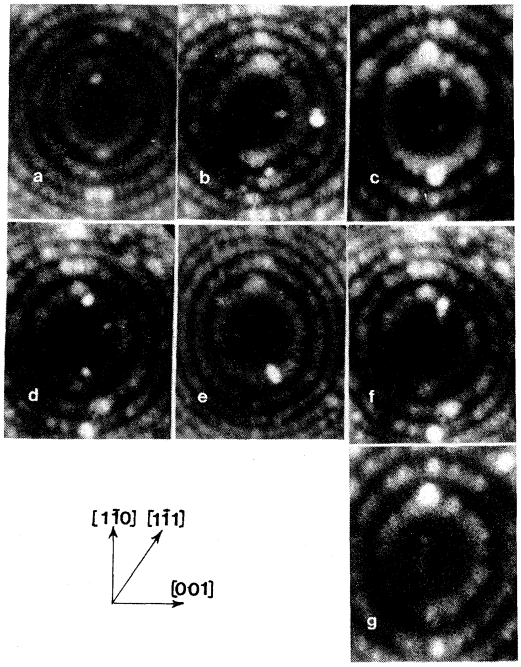


FIG. 1. Helium field-ion images of seven bond configurations observed. These micrographs were taken at approximately (20 – 30)% below the best image field.

adatoms show that the interaction is oscillatory.[7,8] However, no superstructure of a metal adlayer on a metal surface by thermal equilibration, which correlates well with the observed pair energies, has ever been found. In this report we present an observation of a superstructure adlayer of Si atoms on the W{110} which correlates well with the observed Si-Si pair interaction. The observation confirms the theory of adlayer superstructure formation in a most direct manner. This study also represents the first successful FIM study of Si adlayer formation. We have succeeded in obtaining quantitative data on single Si adatom diffusion on the W{110}, and on Si adatom field desorption behavior recently.[9]

Procedures for FIM single-adatom experiments can be found elsewhere.[7,8] We emphasize the rigorousness of our vacuum processings. As the desorption field of Si adatoms was reduced drastically by traces of hydrogen, we used exclusively Vyco-glass–diffused helium for FIM imaging. FIM imagings were done at 78 °K. Si adatoms were deposited by resistivity heating of a stripe of high-purity Si wafer, which had been degassed near the melting point in $10^{-11}$ Torr for 24 h, repeatedly. The impurity concentration of the wafer was $10^{14}$ cm$^{-3}$.

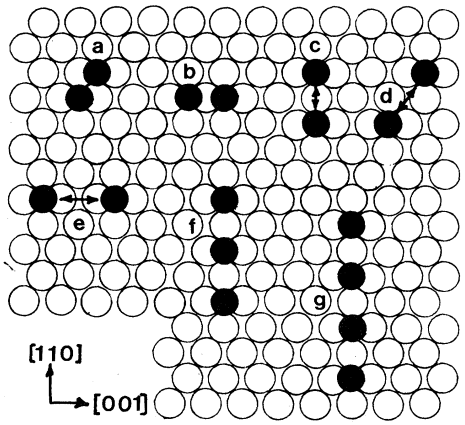


FIG. 2. Structures of the seven bond configurations shown in Fig. 1.

The FIM image of single Si adatoms was so much dimmer than metal adatoms that when a Si adatom was near the center of a {110} plane it was very difficult to be seen. However, no such difficulty existed when they were outside the central region of the plane. The reason for this peculiar imaging property is not clear. It may be due to a lack of field adsorption of image gas atoms because of the small polarizability of Si adatoms, or because of its much smaller size, $r \simeq 1.17$ Å for Si as compared to $r \simeq 1.30$ Å for W. The low image brightness and contrast of Si adatoms when they were near the plane center presented a serious problem for measuring a pair distribution with two Si adatoms on a plane, since it was almost impossible to avoid an accidental field desorption of the Si adatom near the plane edge while trying to search for the other Si adatom which happened to be near the plane center. Because of this imaging behavior, overexposure of films by a factor of 5–10 was needed to bring out the Si adatom images. The low desorption field of Si adatoms necessitated imaging them at

TABLE II. Two-dimensional binding energy per adatom in an adlayer.

| Adlayer structures | Binding energies[a] |
|---|---|
| $1\times1$ | $-41\pm18$ meV |
| $2\times1$ | $-47\pm14$ meV |
| $c(2\times2)$ | $-41\pm18$ meV |
| $(2\sqrt{2}/\sqrt{3}\times4/\sqrt{3})R35.26°$ | $+35\pm7$ meV |

[a]Pair energy of bond configuration $a$ is taken to be the reference level.

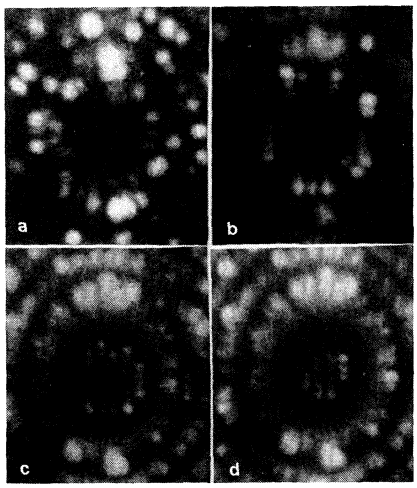


FIG. 3. (a) An "as deposited" Si adlayer. (b) Formation of a superstructure after annealing at 300 °K for 50 sec. (c) and (d) A sequence of field desorption that reveals the structure more clearly.

(15–30)% below the helium best image field. Resolution was slightly compromised. However, images in original film are good enough for making definitive identification of the structures.

Because of the image contrast problem, the study of adatom-adatom interaction was done with three to six Si adatoms on a plane. After adatoms were deposited on a plane, the surface was repeatedly heated to 300 ± 5 °K for 50 sec in field-free conditions. The pair bonds identified and the frequencies of observation are listed in Table I. Field-ion images and the pair structures are shown in Figs. 1 and 2. The statistical weights listed in Table I for various bonds correspond to the number of sites available to an adatom for forming such bonds. As the size of the plane is much larger than the bond lengths in question, the effect of plane boundary is small. The pair energies are derived according to

$$\frac{p(\vec{r}_1)}{p(\vec{r}_0)} = \frac{g(\vec{r}_1)\exp[E_b(\vec{r}_1)/kT]}{g(\vec{r}_0)\exp[E_b(\vec{r}_0)/kT]},$$

where $p(\vec{r})$ is the relative frequency of observation, $g(\vec{r})$ is the statistical weight, and $E_b(\vec{r})$ is the pair binding energy, or the negative value of the pair energy.

The energies listed in Table I show a strong binding between adatoms for the bond configuration $c$, and a strong antibinding for the configuration $b$. Considering statistical uncertainties, configurations $a$ and $e$ have nearly the same energy, while configuration $d$ is slightly repulsive.

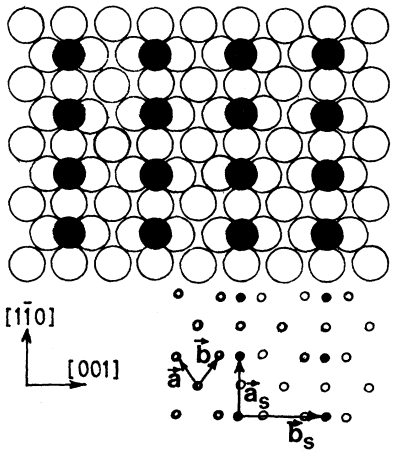


FIG. 4. Structures of the adlayer. $\vec{a}_s$ and $\vec{b}_s$ are lattice vectors of adlayer superstructure.

Although more than two adatoms are present on a plane, the pair energies derived are expected to be reliable within a few percent since another adatom is rarely near a pair in question, and the density of adatoms is very low. The uncertainties come dominantly from statistical errors. Our data, from 515 heating periods of observation, is very large, especially considering the difficulties involved in imaging Si adatoms. To reduce the uncertainty by a factor of 3, one needs 5000 heating periods of observation, which is impractical now.

Even with this amount of data, we were able to predict what kind of a superstructure a Si adlayer on the W{110} should be. Assuming that pair energies for other bonds were small compared to those listed, we found that for the 1×1 structure, the binding energy (BE) per adatom in the adlayer was $-41 \pm 18$ meV (the binding energy of bond $a$ was taken as a reference). The lowest-

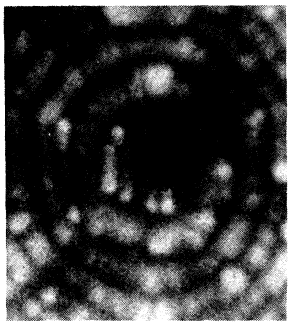

FIG. 5. A field-ion image of growth defects in an adlayer.

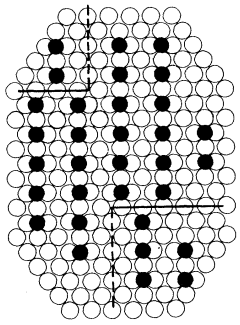

FIG. 6. Structure of the growth defects shown in Fig. 5. Solid lines indicate antiphase domain boundaries. Dashed lines indicate stacking fault lines.

energy structure was the $(2\sqrt{2}/\sqrt{3}\times 4/\sqrt{3})R35.26°$, with a binding energy per atom of $35\pm 7$ meV. Table II lists the BE for various adlayer structures.

Motivated by the argument given above, we searched for the formation of an adlayer superstructure. The experiment consisted of developing a W{110} plane by field evaporation, then depositing a fraction of a monolayer of Si adatoms. After the deposition, the surface was heated to 300 or 310 °K for 50 sec. One period sufficed to form a superlattice since single Si adatoms start to diffuse[9] around 250 °K. Figure 3 shows images of a superstructure formed. The structure was indeed $(2\sqrt{2}/\sqrt{3}\times 4/\sqrt{3})R35.26°$ as predicted. Figure 4 illustrates the structure. We emphasize here that the adlayer superstructure was formed by thermal equilibration of vapor-deposited Si adatoms in field-free conditions. The superstructure could also be formed by heating to 270 °K for 1 min. Further heating to 310 °K for a few minutes did not change the structure, but did change the composites and shape of the adlayer.

Because of the nature of the superstructure one could expect a formation of antiphase domains and stacking faults during the nucleation process of an adlayer. These growth defects were indeed often observed, as shown in Figs. 5 and 6.

In conclusion, we have presented data on pair energies of Si-Si interaction on the W{110} for several bond configurations, showing convincingly a nonmonotonic distance dependence. A superstructure of Si adlayer has been observed. The two data correlate well. This is the first time such correlation has been found in an experimental measurement. This study also represents the first successful direct FIM observation of superstructure formation of adlayers by thermal equilibrium of vapor deposited atoms. Our computer simulations that use the experimental pair energies indeed show the same equilibrium superstructure.

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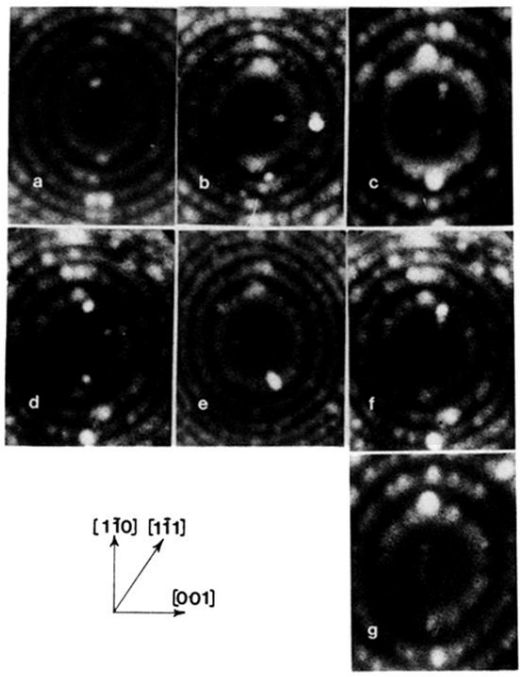


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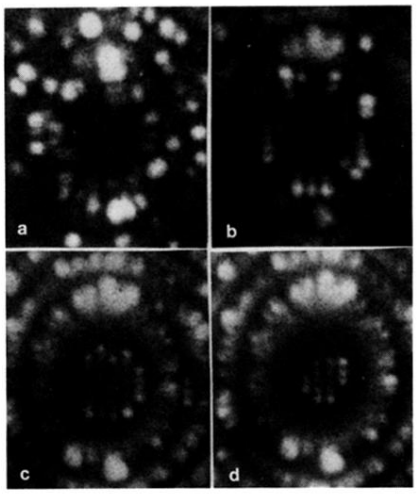


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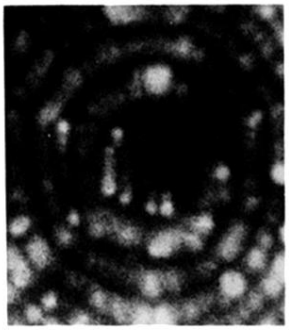

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