Dimer Configuration of Si(001)2×1 Surface by Projected Potential Approach of Reflection High-Energy Electron Diffraction*

Yoshimi Horio[†]

Department of Electrical and Electronic Engineering, School of Engineering,
Daido University, Takiharu-cho 10-3, Minami-ku, Nagoya 457-8530, Japan

Yuji Takakuwa and Schuichi Ogawa

Institute of Multidisciplinary Research for Advanced Materials,
Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980-8577, Japan
(Received 15 December 2013; Accepted 31 May 2014; Published 9 August 2014)

The configuration of asymmetric dimers on the Si(001)2×1 surface was investigated at room temperature (RT) and high temperature (HT) by measurements of many-beam rocking curves of reflection high-energy electron diffraction (RHEED). We propose a novel projected potential approach for analyzing the dynamic structure of the Si(001)2×1 surface, on which high frequency flip-flop of asymmetric dimers occurs. This method is based on reciprocal lattice rods in the 0th Laue zone, which represent Fourier components of the projected crystal potential along the incident azimuth, so that the cross-sectional surface structure that is perpendicular to the incident azimuth can be investigated. It has been confirmed that this approach is effective for such dynamic surface structures with randomly flipping dimers. The asymmetric dimer configuration for the Si(001)2×1 surface at RT was determined to be fundamentally the same as that for the static Si(001)c(4×2) surface. The dimer relaxation into a symmetric configuration was confirmed to occur at a HT of approximately 1000 K.

[DOI: 10.1380/ejsnt.2014.380]

Keywords: Reflection high-energy electron diffraction (RHEED); Surface structure analysis; Si(001)2×1; Asymmetric dimer

I. INTRODUCTION

The Si(001) surface is one of the most extensively studied surfaces with respect to fundamental science and applications. The Si(001) surface is used as a substrate for the growth of thin films and nanodots in electronic and optical device applications. Since the dimer structure of Si(001) was proposed in 1959 in the pioneering work of Schlier and Farnsworth [1], many fundamental structural investigations have been conducted. Recently, the Si(001) surface structure was reported to have an order-disorder phase transition at around 200 K; the c(4×2) surface structure appears at low temperature (LT) under 200 K, while the 2×1 surface structure appears at higher temperatures [2]. Scanning tunneling microscopy (STM) imaging of the c(4×2) surface structure shows zigzag protrusions along the dimer rows [3], which indicate the ordered asymmetric dimers with anti-phase structure. The configuration of the asymmetric dimers is almost clarified, as presented in Refs. [4-7]; the dimer bond length is *ca.* 2.28 Å and the inclination angle is *ca.* 18°.

However, asymmetric dimers on the 2×1 surface structure are known to exhibit flip-flop motion and the configuration is still open to question. The temperature range from 500 to 1000 K is generally utilized for the fabrication of devices on Si(001) substrates. Clarification of the 2×1

FIG. 1. Experimental setup.

surface structure is therefore important in this sense. Not only does high-frequency flip-flop motion of asymmetric dimers occur on the Si(001)2×1 surface, but a mixture of 2×1 and 1×2 domains is also present. The direction of dimer rows in one domain is perpendicular to that in an adjacent domain. Such a dynamic double-domain structure makes a detailed structural analysis difficult, in contrast to the static c(4×2) surface structure. This may be the reason that there has been little progress in the structural analysis of the 2×1 surface at room temperature (RT) and high temperature (HT).

The Si(001)c(4×2) surface has energetically stable asymmetric dimers [8] at LT. When the temperature rises above 200 K, the asymmetric dimers begin a flip-flop motion and the 2×1 surface appears. There are some reports on the RT 2×1 surface structure analyzed using experimental methods such as reflection high-energy electron diffraction (RHEED) [9] and surface X-ray diffraction (SXRD) [10], and theoretically by first-principles calculations [11]. Takahashi *et al.* [10] measured SXRD rocking curves for fractional order spots at RT and analyzed the 2×1 surface structure with relaxation of up to six layers. Fukaya and Shigeta [9] measured one-beam RHEED

* This paper was presented at the 12th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures (ACSIN-12) in conjunction with the 21st International Colloquium on Scanning Probe Microscopy (ICSPM21), Tsukuba International Congress Center, Tsukuba, Japan, 4-8 November, 2013.

[†] Corresponding author: horio@daido-it.ac.jp

FIG. 2. Configuration of asymmetric dimer of Si(001) surface; (a) plan view of the Si(001) $c(4 \times 2)$ surface, (b) and (c) projected structures along $[1-10]$ and $[110]$ azimuths, respectively. (d) and (e) show the structure parameters for the relaxation of asymmetric dimer in 1×1 square lattice viewing from the top and side, respectively.

rocking curves, which were used to analyze the depth position of each atomic layer and the dependence on temperature from RT to 1650 K. According to the one-beam RHEED analysis results, asymmetric dimers transform to symmetric dimers at around 900 K followed by melting at over 1440 K [12,13]. In addition, a semiconductor-metal transition occurs around 900 K [14], which suggests a correlation with the structural transition. Structural analysis of the Si(001) 2×1 surface using RHEED has only been conducted using a one-beam approach [9,15] until now.

We have examined the Si(001) 2×1 surface structure at RT and HT (880 and 1031 K) by measuring many-beam RHEED rocking curves. For such a dynamic surface, we have proposed a projected potential approach. It is the first time to use this approach for the dynamic surface of Si(001) 2×1 , on which upper and lower atoms of asymmetric dimers are irregularly replaced at high frequency. Such a dynamic surface can be treated with respect to the projected potential, which superimposes two conditions of time averaged upper and lower atoms of the asymmetric dimer. In the calculation of the diffracted beam intensity, we have focused on the reciprocal lattice rods on the 0-th Laue zone. These rods represent Fourier components of the projected potential along the incident azimuth. The RHEED intensity is strongly influenced by these rods, especially at grazing incidence. The rocking curves were calculated by the multi-slice dynamical theory [16] including these limited reciprocal rods. If the effectiveness of this approach is confirmed, then more information on dynamic surface structures that change by an increase in temperature from RT to HT can be acquired than that by the one-beam approach. The one-beam approach can ob-

tain only the depth (one-dimensional) positions of atoms, whereas the projected potential approach can obtain the two-dimensional positions of atoms on the cross section that is perpendicular to the incident azimuth. As a result of such an analysis, the dimer configuration of the Si(001) 2×1 surface has been obtained at RT and HT.

II. EXPERIMENTAL

The experiment was conducted using an ultrahigh-vacuum (1×10^{-7} Pa) RHEED apparatus. An n -type (P-doped) Si(001) single crystal ($3 \times 15 \times 0.5$ mm³) with a resistivity of 1-10 Ω cm was used as the sample. The commercial Si(001) sample surface, which is cut within $\pm 0.1^\circ$ accuracy from a (001) plane, generally consists of double domain terraces separated by single atomic steps. The sample surface was repeatedly cleaned by direct current heating up to *ca.* 1200 $^\circ$ C in the ultra-high vacuum and then a high contrast RHEED pattern of the 2×1 super structure with double domains appeared.

Figure 1 shows a schematic diagram of the experimental setup. The electron gun used can be mechanically tilted using a stepping motor and diffracted electron beam intensities are automatically measured while changing the glancing angle θ of the incident electron beam. The rate of the glancing angle change was *ca.* $2.7^\circ/\text{min}$. Rocking curves of the peak intensities of the diffraction spots were measured using a CCD camera with an interval of *ca.* $\theta = 0.05^\circ$. The acceleration voltage of the electron beam was 10 kV and the incidence azimuth was set at $[1-10]$.

Rocking curves were measured at RT and HT. At HT, the Si(001) sample was heated at 880 and 1031 K by passing currents of 0.5 and 1.4 A, respectively. The temperature was measured with an infrared radiation thermometer (IR-CAT1CS, Chino Corp.).

III. CALCULATION

Figure 2 shows a plan view of the Si(001) $c(4\times 2)$ surface, and projected structures along the $[1-10]$ and $[110]$ azimuths. The periodicity of 4×2 becomes that of 2×1 by viewing from the projected structures. In the projected potential approach, the phase of the buckling in an asymmetric dimer row is ignored. It is expected that this projected potential approach is very effective for such surface structural analysis accompanied with dynamic flip-flop motion of the asymmetric dimers. The dynamic Si(001) 2×1 surface structure with flip-flop motion can be treated as a static surface structure, where the flipping up and down Si atoms of the asymmetric dimers are superimposed on each other.

The structure parameters of the asymmetric dimer are presented in Figs. 2(d) and 2(e). Two Si atoms in the first layer denoted as A and B construct the dimer, and four Si atoms in the second layer denoted as C, C', D and D' are also shown. The upper atom A of the asymmetric dimer connects to the second layer C and C' atoms. Similarly, the lower atom B connects to the second layer D and D' atoms. The length of an edge of the 1×1 square lattice is denoted by a_0 ($a_0 = 3.84$ Å) and the ideal (bulk truncated) position of atom C is defined as the origin in three-dimensional space. The depth position of the second layer is fixed at zero. The positions of the A and B dimer atoms are expressed as (a_x, a_y, a_z) and (b_x, b_y, b_z) . The height difference associated with buckling between the A and B dimer atoms is expressed by $a_z - b_z$, and the inclination angle α of the dimer bond is $\alpha = \sin^{-1}(a_z - b_z)/r_{AB}$, where r_{AB} is the dimer bond length. For the asymmetric dimer, atom A is pulled up and atom B is pushed down, which is an energetically favorable configuration. This atomic arrangement affects the positions of the second layer atoms. Deviations along the x - and y -axis directions from the ideal position of the second layer C atom are expressed by Δc_x and Δc_y , respectively. Deviations are similarly expressed for the other second layer atoms of C', D and D'.

The distance along the x -axis between C and D, denoted as x_{CD} , is obtained from $x_{CD} = a_0 - \Delta c_x - \Delta d_x$, and similarly $x_{C'D'} = a_0 - \Delta c'_x - \Delta d'_x$. The distance along the y -axis between C and C', denoted as $y_{CC'}$ is obtained from $y_{CC'} = a_0 - \Delta c_y - \Delta c'_y$, and similarly $y_{DD'} = a_0 + \Delta d_y + \Delta d'_y$. Here $x_{CD} = x_{C'D'} < a_0$ and $y_{CC'} \leq a_0 \leq y_{DD'}$.

Recent structural models for the $c(4\times 2)$ surface, which were deduced from several methods such as correlated thermal diffuse scattering (CTDS) [4], total energy calculation [5], photoelectron diffraction (PED) [6], and SXRD [7], are in relatively good agreement, as shown in Table I. The structure parameters reported in Refs. [4-6] are very close to each other. Therefore, the x -axis deviations of the second layer atoms were assumed to be fixed values, $\Delta c_x = \Delta c'_x = \Delta d_x = \Delta d'_x = 0.12$ Å, which are

FIG. 3. Changes of the structure parameters of dimer atoms A and B depending on the relaxation parameter R . Here, a_x (b_x) and a_z (b_z) indicate x and z coordinates of dimer atom A (B), respectively. a_0 is the lattice constant (3.84 Å) of 1×1 square lattice and α the inclination angle of the dimer bond.

the same as those given in Ref. [5]. The other structure parameters are also fixed, such as the dimer bond length $r_{AB} = 2.28$ Å, $a_y = b_y = a_0/2 = 1.92$ Å, and all the back bond lengths $AC = AC' = BD = BD' = 2.33$ Å. These values are similar to the averaged values among the results of Refs. [4-6]. The locations of Si atoms under the second layer were set at their ideal positions for simplicity. These structure parameters are shown in the last line of Table I and are used for the rocking curve calculations of the Si(001) 2×1 surface at RT performed in this study.

The surface configuration is known to change from asymmetric dimers to symmetric dimers with an increase in temperature from RT to HT. Here, the following relaxed asymmetric dimer model was considered. It was assumed that all the lengths of the dimer bonds and the back-bonds were fixed (see previous paragraph), but only the bond angles were allowed to be changed for stability of the surface energy. The upper atom A of the dimer is inclined downward and the lower atom B is inclined upward, as shown by the arrows in Fig. 2(e). In the top view in Fig. 2(d), the top dimer A and B atoms shift to the right-hand side ($[110]$ direction), as shown by arrows. The second layer C and C' atoms shift outward and the D and D' atoms shift inward along the y -axis, as shown by the arrows, to maintain their x components, such as $\Delta c_x = \Delta c'_x = \Delta d_x = \Delta d'_x = 0.12$ Å.

A relaxation parameter R ($0 \leq R \leq 1$) was newly introduced to evaluate such relaxation of the asymmetric dimer. It was simply assumed that the structure parameters of a_x , $\Delta c_y (= \Delta c'_y)$ and $\Delta d_y (= \Delta d'_y)$ vary linearly with R , i.e., $a_x = 0.65 + 0.13 \cdot R$ and $\Delta c_y = \Delta d_y = 0.12 \cdot (1 - R)$. When the relaxation parameter R is given, the structure parameters of a_x , $\Delta c_y (= \Delta c'_y)$ and $\Delta d_y (= \Delta d'_y)$ are determined according to these formulas, and then a_z , b_x and b_z are calculated under the condition of fixed bond lengths. The structure parameters for $R = 0$ correspond to the asymmetric dimer configuration associated with $c(4\times 2)$, which is shown in the last line of Table I, and those for $R = 1$ correspond to the symmetric dimer configuration with $a_z = b_z = 1.14$ Å and $a_x = a_0 - b_x = 0.78$ Å. When R is between 0 and

TABLE I. Structure models deduced from several researches.

	α (deg)	r_{AB}	a_z	b_z	x_{CD}	$y_{CC'}$	$y_{DD'}$
CTDS[4]	18 ± 1	2.28	1.37	0.75	3.55	3.63	4.03
Theory[5]	18.8	2.29	1.39	0.65	3.60	3.60	4.08
PED[6]	18.6 ± 1	2.26	1.36	0.64	3.64	3.74	3.94
SXRD[7]	20 ± 3	2.67	1.67	0.75	3.7	3.84	3.84
Present	18.1	2.28	1.38	0.67	3.60	3.60	4.08

1, the structure parameters correspond to an intermediate stage of the relaxed asymmetric dimer configuration. The values of the a_x , a_z , $a_0 - b_x$, and b_z structure parameters and the inclination angle α change with R , as shown in Fig. 3. The height difference between the asymmetric dimer atoms A and B, 0.71 Å, becomes 0 Å with the change from $R = 0$ to $R = 1$.

The multi-slice method [16] was used for calculation of the diffraction intensities, and the crystal surface was sliced in a parallel manner up to a depth of *ca.* 100 Å with a thickness interval of 0.1 Å. An atomic scattering potential was obtained from the analytical formula [17], and 10% of the value was adopted as an imaginary potential for the incident beam absorption effect. The Debye-Waller factor was calculated using the Debye temperature of Si (580 K [18]), which corresponds to the averaged vibration amplitude of a Si atom, 0.07 Å at RT, 0.12 Å at 880 K, and 0.13 Å at 1031 K. For the incidence azimuth [1-10], the number of reciprocal lattice rods that were introduced into the calculation was 13 in the 0-th Laue zone, i.e., 0 0, $\pm 1/2$ 0, ± 1 0, $\pm 3/2$ 0, ± 2 0, $\pm 5/2$ 0 and ± 3 0. Each reciprocal lattice rod in the 0-th Laue zone corresponds to the Fourier coefficient of the crystal potential projected along the [1-10] incidence azimuth. The projected structure of the crystal cross section determines the diffracted spot intensities in the 0-th Laue zone. The anti-phase structures of upper and lower atoms along the asymmetric dimer rows overlap with each other. In this situation, there is no difference among the $c(4 \times 2)$, $p(2 \times 2)$ and 2×1 structures. Here, the 2×2 unit mesh was considered in the calculations.

Many monatomic steps are present on a commercial Si(001) sample surface, and the directions of dimer rows are thus orthogonal to each other on the adjacent upper and lower terraces, i.e., a double-domain surface where the 2×1 structure coexists with the 1×2 structure. The rocking curve calculation must consider such double domains. Therefore, the calculations were conducted not only at the [1-10] incidence (Fig. 2(b)), but also at [110] incidence (Fig. 2(c)). The calculated results were summed, not with respect to coherency but to intensity, because the averaged terrace width is considered to be almost equal to or larger than the coherence length for the incident electron beam. Here, the terrace areas of 2×1 and 1×2 domains were treated as equal to each other because of the similar intensity of each half-order spot reflected from each domain.

The number of reciprocal lattice rods used in the rocking curve calculations at [110] incidence was also 13, i.e., 0 0, $0 \pm 1/2$, 0 ± 1 , $0 \pm 3/2$, 0 ± 2 , $0 \pm 5/2$ and 0 ± 3 on the 0-th Laue zone. In this [110] incident azimuth, the half order spots disappear because there is no super (two times) periodicity in the atomic arrangement, as shown in the side

view of Fig. 2(c). In the calculated rocking curve for the double domain surface, the integer order spot intensity is an addition of the calculated results for both the [1-10] and [110] azimuths; however, the half-order spot intensity reflects only the calculated result for the [1-10] azimuth.

IV. RESULTS AND DISCUSSION

Representative calculated rocking curves for five diffraction spots, 0 0, $1/2$ 0, 1 0, $3/2$ 0 and 2 0, at $T = 1031$ K are shown in Fig. 4 for each stage of the relaxed asymmetric dimer. When the relaxation parameter R increases from 0.0 (asymmetric dimer) to 1.0 (symmetric dimer), the rocking curves for the five spots have the following characteristics. The significant features are indicated by arrows in Fig. 4.

- 1) For the 0 0 spot, two Bragg peaks at approximately $\theta = 1.9^\circ$ and $\theta = 3.3^\circ$ increase in intensity; however, the shoulder peak at $\theta = 3.1^\circ$ becomes weak.
- 2) For the $1/2$ 0 spot, the peak at $\theta = 2.5^\circ$ weakens.
- 3) For the 1 0 spot, the relative intensity of the two peaks at $\theta = 2.7^\circ$ (arrow B) and at $\theta = 3.1^\circ$ (arrow A) is inverted. This feature is effective for evaluating the stage of relaxation for the asymmetric dimer.
- 4) For the $3/2$ 0 spot, no significant changes are observed.
- 5) For the 2 0 spot, the intensities of both peaks at $\theta = 3.8^\circ$ and $\theta = 4.1^\circ$ are increased.

Figure 5 compares the five experimental rocking curves for 0 0, $1/2$ 0, 1 0, $3/2$ 0 and 2 0 spots measured at RT with those calculated for $R = 0$ (asymmetric dimer). The experimental rocking curves were best fitted by the calculated curves when $R = 0$ compared with other values of R . The dimer configuration on the Si(001) 2×1 surface at RT was confirmed to be fundamentally the same as that on the static $c(4 \times 2)$ surface, except for the flip-flop motion. In addition, the projected potential approach was verified as an effective method for the structural analysis of such dynamic surfaces.

The experimental peaks are generally slightly broader than the calculated peaks, which may be due to the small divergence angle of the incident electron beam. The experimental intensity was weaker than the calculated intensity near the spot emergence, which may be due to the following effects near the shadow edge. When the diffracted electron beam exits through the vicinity of the sample surface, it suffers atomic step scatterings and surface plasmon losses, the effects of which decrease the beam

FIG. 4. Changes of rocking curves of five spots for each stage of relaxed asymmetric dimer from $R = 0.0$ to $R = 1.0$. Arrows indicate the remarkable peak positions.

intensity. For example, the experimental $0\ 0$ beam intensity was weaker than the calculated intensity around $\theta = 1^\circ$, and the experimental $1\ 0$ beam intensity that emerges at $\theta = 1.9^\circ$ is weaker than that calculated at around $\theta = 2.0^\circ$.

Some of the rocking curves have peaks at 004 ($\theta = 1.66^\circ$), 006 ($\theta = 3.34^\circ$), 008 ($\theta = 4.79^\circ$), 224 ($\theta = 3.33^\circ$), 226 ($\theta = 4.31^\circ$), and 228 ($\theta = 5.48^\circ$) Bragg reflection conditions. Each glancing angle for the Bragg reflection is calculated using the mean inner potential of Si (12 eV). The glancing angle $\theta = 1.7^\circ$ for the 004 Bragg peak shifts to a higher angle of $\theta = 2.0^\circ$. The reason is considered to be that such a low glancing angle is surface sensitive and the surface reconstruction containing the dimers prevents the regular 004 Bragg reflection. The 006 Bragg reflection is generally forbidden for bulk diamond crystal; however, the 006 reflection is not explicitly forbidden for a limited surface region; the glancing angle of $\theta = 3.34^\circ$ is almost overlapped with that of the intense 224 Bragg reflection at

FIG. 5. Comparison between experimental (thick lines) and calculated (thin lines) rocking curves at RT. The calculated rocking curves are the best fitted ones with $R = 0.0$.

$\theta = 3.33^\circ$. In addition, there are many minute peaks that cannot be explained by simple Bragg reflections, which may be due to multiple scattering effects.

At high temperatures of 880 and 1031 K, the configuration of the asymmetric dimer is analyzed with particular attention to the relative peak intensities at $\theta = 3.1^\circ$ (arrow A) and $\theta = 2.7^\circ$ (arrow B) in the rocking curve for the $1\ 0$ spot, as shown in Fig. 4. Peak A is dominant at RT, whereas the intensity of peak B increases in contrast to peak A when the temperature becomes higher, as shown in Figs. 5 and 6. Thus, the asymmetric dimer becomes relaxed toward the symmetric configuration at higher temperature. As a result, the R values that give the best agreement with the experimental rocking curve are determined to be 0.3 and 0.5 for 880 and 1031 K, respectively. The calculated rocking curves for the fractional order spots, $1/2\ 0$ and $3/2\ 0$, reproduce the experimental curves well; however, the calculated peak intensity of the specular spot at $\theta = 2.0^\circ$ is especially weak compared with the experimental intensity. This may be due to the slight relaxation of subsurface layer atoms under the dimers; however, this is not considered here for simplicity.

The relaxed asymmetric dimer does not achieve the symmetric configuration, even at 1031 K. This is not in agreement with the result obtained by one-beam RHEED analysis [9], which concludes that asymmetric dimers change into the symmetric dimers at around 900 K. A possible interpretation for this contradiction is considered to be a mixed dimer. When asymmetric dimers ($R = 0.0$) make up 30% of the surface area and sym-

FIG. 6. Comparison between experimental (thick lines) and calculated (thin lines) rocking curves at (a) 880 K (b) 1031 K. The calculated rocking curves are the best fitted ones with (a) $R = 0.3$ and (b) $R = 0.5$.

metric dimers ($R = 1.0$) make up 70%, then the calculated rocking curves reproduce the experimental results as well as those with in Fig. 6(b). In this case, the 30% area with asymmetric dimers may exist near step edges or defects. The ratio of asymmetric to symmetric dimer coverage may depend on the conditions used for cleaning and surface preparation.

V. CONCLUSIONS

The surface structure of Si(001)2×1 observed at RT and HT was analyzed using an averaged potential approach of many-beam RHEED. The results indicate that the Si(001)2×1 surface at RT is made up of asymmetric dimers, which is basically the same configuration as that for the $c(4\times 2)$ surface. The height difference between the upper and lower Si atoms of the asymmetric dimer, $a_z - b_z$, is 0.71 Å and the inclination angle of the dimer bond, α , is 18.1°, as shown in Table I. The height difference associated with buckling, $a_z - b_z$, is similar to the value of 0.87 Å deduced from SXRD measurements [10] and the value of 0.6 Å deduced by the one-beam RHEED method [15]. The projected potential approach was confirmed to be effective for structural analysis of a dynamic surface on which flip-flop motion of dimers occurs at high frequency. This approach has already been used for the structural analysis of static multi-domain crystal surfaces [19]; however, this study is the first to analyze the dynamic surface structure with this approach.

At a temperature of 880 K, relaxed asymmetric dimers

with $R = 0.3$ reproduce the experimental rocking curves well. The height difference associated with buckling, $a_z - b_z$, decreases to 0.43 Å and the inclination angle becomes gentle at $\alpha = 10.9^\circ$. This height difference is slightly larger than the result of 0.25 Å deduced using one-beam RHEED [9] at 773 K.

At a temperature of 1031 K, the presence of further relaxed asymmetric dimers with $R = 0.5$ was deduced from the rocking curve analysis. The height difference associated with buckling was 0.29 Å with $\alpha = 7.4^\circ$. This result disagrees with that obtained from a one-beam RHEED analysis [9], which concluded that the asymmetric dimer became symmetric at around 900 K. To avoid this contradiction, another possibility is considered to be the coexistence of asymmetric and symmetric dimers on the surface. A Si(001)2×1 surface, on which 30% of the area is occupied by asymmetric dimers with $R = 0.0$, and 70% by symmetric dimers with $R = 1.0$, can also reproduce the experimental results as well as the relaxed asymmetric dimer with $R = 0.5$. The remaining asymmetric dimers are considered to be fixed near step edges or defects and the ratio of the asymmetric to symmetric dimer area may depend on the surface condition. As a conclusion, it has been clarified that asymmetric dimers tend to relax into symmetric dimers at around 1000 K.

ACKNOWLEDGMENTS

This work was performed under the Cooperative Research Program of "Network Joint Research Center for

Materials and Devices” and was supported by JSPS KAK- ENHI Grant Number 25390085.

-
- [1] R. E. Schlier and H. E. Farnsworth, *J. Chem. Phys.* **30**, 917 (1959).
 - [2] T. Tabata, T. Aruga, and Y. Murata, *Surf. Sci.* **179**, L63 (1987).
 - [3] R. A. Wolkow, *Phys. Rev. Lett.* **68**, 2636 (1992).
 - [4] T. Abukawa, C. M. Wei, K. Yoshimura, and S. Kono, *Phys. Rev. B* **62**, 16069 (2000).
 - [5] A. Ramstad, G. Brocks, and P. J. Kelly, *Phys. Rev. B* **51**, 14504 (1995).
 - [6] R. Gunnella, E. L. Billock, L. Patthey, C. R. Natoli, T. Abukawa, S. Kono, and L. S. O. Johansson, *Phys. Rev. B* **57**, 14739 (1998).
 - [7] F. Felici, I. K. Robinson, C. Ottaviani, P. Imperatori, P. Eng, and P. Perfetti, *Surf. Sci.* **375**, 55 (1997).
 - [8] D. J. Chadi, *Phys. Rev. Lett.* **43**, 43 (1979).
 - [9] Y. Fukaya and Y. Shigeta, *Phys. Rev. Lett.* **91**, 126103 (2003).
 - [10] M. Takahashi, S. Nakatani, Y. Ito, T. Takahashi, X. W. Zhang, and M. Ando, *Surf. Sci.* **338**, L846 (1995).
 - [11] M. J. Yin and M. L. Cohen, *Phys. Rev. B* **24**, 2303 (1981).
 - [12] J. J. Metois and J. C. Heyraud, *Surf. Sci.* **446**, L127 (2000).
 - [13] A. Santoni, V. R. Dhanak, L. Grill, and L. Petaccia, *Surf. Sci.* **474**, L217 (2001).
 - [14] L. Gavioli, M. J. Betti, and C. Mariani, *Phys. Rev. Lett.* **77**, 3869 (1996).
 - [15] T. Makita, S. Kohmoto, and A. Ichimiya, *Surf. Sci.* **242**, 65 (1991).
 - [16] A. Ichimiya, *Jpn. J. Appl. Phys.* **22**, 176 (1983).
 - [17] P. A. Doyle and P. S. Turner, *Acta Crystallogr. A* **24**, 390 (1968).
 - [18] G. Radi, *Acta Crystallogr. A* **26**, 41 (1970).
 - [19] A. Ichimiya and Y. Ohno, *Surf. Rev. Lett.* **4**, 985 (1997).