Si(100)表面－位相欠陥のダイナミックスと構造相転移

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Abstract: Dynamics of a new movable type P phase defect, that is, phasons formed on Si(100) dimer rows, and related structural changes were studied from room temperature to 6K on an atomic scale, in relation to the interaction between Si(100) surface dimers. At ～200K, dimer flip-flop motion began to freeze from the defects on dimer rows, and the antiferomagnetic correlation appeared along dimer rows first. With further decrease in temperature, c(4x2) structure began to cover the surface. While type P defects migrated on the surface, the c(4x2) arrangement persisted as the temperature decreased to 30K. The observed change was consistent with the order-disorder phase transition which has been observed on the Si(100) surface. At 6K, in contrast, the migration of the phasons resulted in an apparent phase transition between c(4x2) and p(2x2) arrangements, which indicates that the interaction between dimer rows is significantly weaker at this temperature, and suggests some characteristic change between 30K and 6K. Long range interaction was found to play an important role on Si(100) surface.

With the progress of the nanoscale science and technology, atomic defects in material surfaces/ interfaces begin to play an increasingly important role, and therefore it is necessary to characterize the structure of the defects at an atomic scale. For the Si(100) surface, it is well established that pairs of top-layer atoms form dimers. As identified by Hamers et al., there are three typical types of defects: type A corresponding to a single dimer vacancy; type B to a double dimer vacancy; and type C to two half-dimers resulting from two adjacent Si vacancies along the <110> direction [1]. Recently, a new type of movable defect known as type P defect, was found to exist on the Si(100) surface, and the dynamics of the phase defect, the phason, was directly observed by scanning tunneling microscopy (STM) at 80K and 6K [2-5]. The type P defect has a structure similar to the type C defect which acts to induce a phase shift; a type P defect consists of two adjacent dimers which are buckled with the same orientation. However, in contrast to the type C defect, type P defect can migrate along dimer rows due to dimer flip-flop motion at the phase boundaries. In this paper, the recent STM studies on these defects will be summarized, and the characteristics of the type P defect, in relation of the interaction between Si(100) surface dimers will discussed.

For defects of types A and B, structural models which have rebonded configurations in the second layer were proposed originally [6]. The electronic structure of the type A defect and the cross section of the type B defect determined by STM at room temperature were considered to provide the evidence for the applicabilities of the rebonded model [7,8]. However, recently, the effects of these defects on the buckling of adjacent dimers were studied by STM at 80K, which raised questions related to the structures of these defects [9]. From the STM observations of Si(100) surfaces at room temperature, type A and type B defects did not cause detectable static buckling of adjacent dimers. At 80K, out-of-phase buckling of adjacent dimers was observed in the case of the double vacancy defect (type B). However, the single vacancy defect (type A) was found to be further subdivided into three types, A1, A2, and A3: A1 suppresses buckling of adjacent dimers even at low temperatures, A2 induces in-phase buckling, and A3 induces out-of-phase buckling. If these three effects are due to differences in the structures of the type A defects, there must be three different internal structures for the type A defect. Details were studied by observing the bias-dependent STM images, and type A and type B defects were found to have a characteristic relationship between their electronic structures and their effects on buckling of adjacent dimers induced at 80K. The relationship between the phase of dimer buckling and the electronic structure of the defect could be comprehensively explained in terms of the dimer structure of the defect [10].

Regarding the type C defect, since from the results of the spectroscopic study only this defect showed a strong metallic character it is considered to form a surface state which causes Fermi level pinning [1]. A structural model with dimer formation in the second layer was proposed by Uda et al. [11]. Since the calculated electronic structure of the type C defect was in good agreement with the STM results, the structure of the type C defect was considered to have been completely determined. However, recently, semiconductive property was observed to be induced at 80K [12]. In addition, single type C defect was found to induce a long range interaction on the surface; when the type C defect was removed by the atomic manipulation technique, the structure of the large area surrounding the defect was observed to be strongly affected [13]. These results are related to the fact that type C defect induces a phase shift, and strong interaction between the type C defect and the surrounding buckled dimers was observed directly [13].

From the experimental results described above, defects of types A, B and C must play a much more important role in the nanoscale technology than expected. Therefore, more detailed analysis is required to clarify their characteristics. In any case, it is clear that phase shift induced in the buckled dimer arrangement by the defects is quite important on the surface. On the other hand, as described above, type P defect is a movable phase defect, and migration of the defects is strongly related to the characteristics of the Si(100) surface structure. However, little is known about the type P defect. In this paper, we present our recent results on the STM observation of the dynamics of the Si(100) surface caused by the type P defect from room temperature to 6K, by focusing on the interaction between dimers on the surface.

As is well known, the details of the dimer arrangement have been controversial during the last two decades. Namely, dimers give rise to the symmetric (2x1) structure; however, the (2x1) phase is not the Si(100) ground state, and different reconstructions within similar dimer structures were proposed [14]. An energetically favored alternation of dimer buckling along the dimer rows leads to the c(4x2) reconstruction, in which alternating buckling angles are also present between two neighboring dimers belonging to different rows. Another possible phase is the p(2x2) phase, in which the buckling angle is the same between two neighboring dimers belonging to different rows. Figure 1 shows a schematic of (a) symmetric 2x1, (b) c(4x2), (c) p(2x2), and (d) coexisting c(4x2) and p(2x2) structures with a single type P defect. Here, only the upper Si atoms of the buckled dimers are illustrated using circles. Lines between the circles are drawn in order to compare the phase shift. In Fig. 1, the antiferomagnetic arrangements of the buckled dimers, which forms a zigzag structure along the dimer rows, shows the out-of-phase (Fig. 1(b)) and in-phase (Fig. 1(c)) relationships between dimer rows for c(4x2) and p(2x2) structures, respectively.

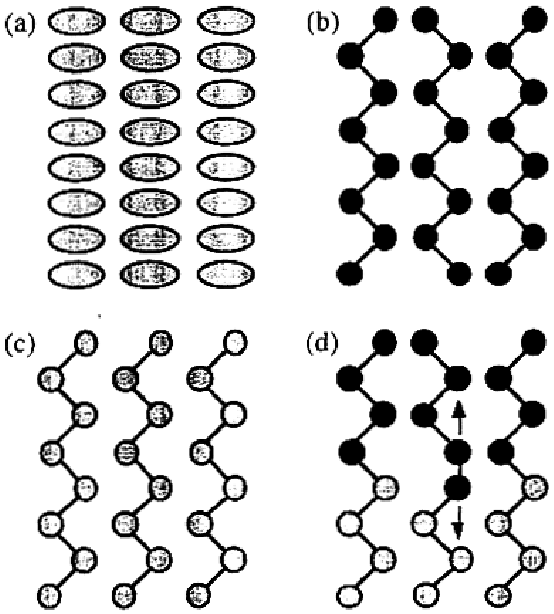

Fig. 1 Schematic of (a) symmetric 2x1, (b) c(4x2), (c) p(2x2), and (d) coexisting c(4x2) and p(2x2) structures with a single type P defect.

What makes the argument more complicated is that the difference between the energies of the p(2x2) and c(4x2) reconstructions obtained by theoretical calculations is only on the order of 1 meV per dimer [14]. From LEED measurements, a reversible phase transition occurs between the ordered c(4x2) and disordered phases at ~200K [15] and the most stable phase was concluded to be c(4x2). Based to the recent low-temperature STM studies at ~ 100K on the surface, the c(4x2) structure was also confirmed to be the most stable arrangement of the buckled dimers [16-18]. These results were thought to have resulted the controversy, however, more recently, the p(2x2) structure was found to reemerge at a lower temperature of ~ 6K, and fluctuations between the c(4x2) and p(2x2) structures was directly observed by STM [2].

The observed phenomenon at ~6K is understood to be caused by the dynamics of the movable phase defects formed on the dimer rows, that is, type P defects. Since type P defects cause a phase shift, when a type-P defect changes its position, apparent phase transition between the c(4x2) and p(2x2) structures occurs (Fig. 1(d)). Existence of a similar defect was confirmed even at room temperature, and the stability of the c(4x2) structure and the origin of the symmetric dimers were comprehensively explained by the dynamics of the phase defect [5]. On the other hand, type P defects tend to form pairs at 80K so as to reduce the area of the p(2x2) arrangement [3], which differs from the characteristic property of the type P defect at 6K; those move more independently of each other at 6K [2]. Therefore, in order to understand the observed change on the Si(100) surface; (1) >150K: disorder (c(4x2) + p(2x2)) → (b) ~ 150K: c(4x2) → (c) ~ 6K: c(4x2) + p(2x2), it is necessary to study the temperature-dependence of the surface dynamics in more detail.

Experiments were performed using a low-temperature STM, which allows observation with atomic resolution at ~6K in ultrahigh vacuum ($5x10^{-9}$Pa). A phosphorus-doped (0.01 Ω cm) Si(100) sample surface was heated upto ~ 1200℃ after prebaking for one day, and cooled very slowly to reduce the density of the surface defects. Base pressure was ~1.0×10^{-8} Pa, and pressure during the heat treatment was kept below ~ 5×10^{-8} Pa.

Figure 2 shows STM images taken at (a) room temperature, (b) ~ 200K, (c) ~ 80K, (d) 30K, and (e) ~ 6K. As is shown in Fig. 2(a), dimers appear symmetric at room temperature as is well known. It is widely accepted that dimers are buckled even at room temperature, and switch back and forth between the two possible orientations in a time much shorter than the time scale of the STM measurement, which results in the observed symmetric configuration in the STM images. However, when the dimers flip-flop without correlation, the flip-flop motion implies a completely disordered surface. On the other hand, when the phase defects migrate rapidly compared to the time scale of STM measurement, symmetric dimers can be formed without completely destroying the 2x anti correlation arrangement, which agrees well with the fact that the electronic structure obtained by photoemission spectroscopy at room temperature is consistent with the theoretical result calculated under the assumption of ordered asymmetric dimers [19]. Considering these results, the symmetric dimers in the Si(100) surface are considered to be caused by the characteristic properties of the type P phase defect of the dimer rows [5]. Some dimers near defects are buckled, which is understood to be caused by the effect of the defects; buckling phase is fixed by the defects.

At ~200K, as shown in Fig. 2(b), buckled dimers frozen near the defects are longer compared to those frozen at room temperature. Even at ~ 200K, buckled dimers are localized near the defects on the dimer rows. In Fig. 2(b), symmetric dimer regions are caused by the migration of the type P defects as described above. From the results at 200K and at room temperature, interaction between dimers is concluded to be stronger along the dimer rows compared to that between dimer rows at this temperature range.

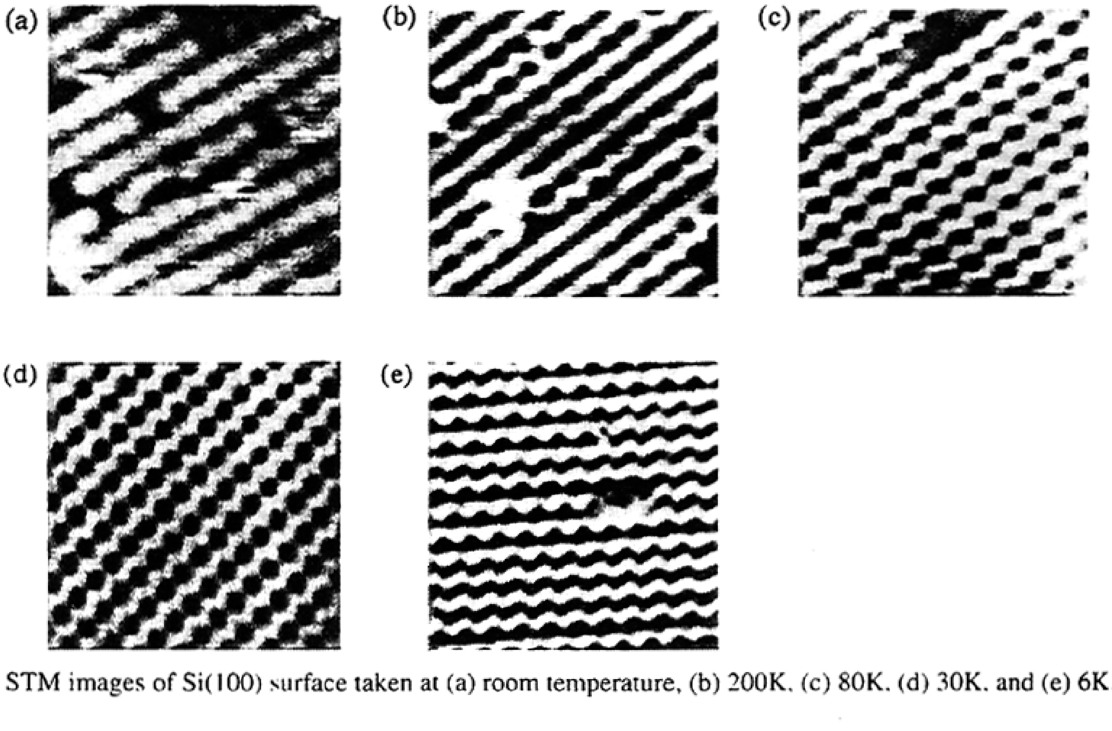

Fig. 2 STM images of Si(100) surface taken at (a) room temperature, (b) 200K, (c) 80K, (d) 30K, and (e) 6K.

According to the previous STM measurement at 144K [16], an ordered c(4x2) structure was observed to cover the surface. In this case, symmetric dimer domains were observed on one side of the type C defects. Since a type C defect produces a phase shift, and introduces an antiphase domain on one of its sides, the observed result indicates that a domain with the complete p(2x2) arrangement with the two adjacent dimer rows is very unstable at 144K. In the STM image obtained at 120K, the p(2x2) arrangement was observed at domain boundaries [17], which indicates that the p(2x2) arrangement which exists at the boundaries is stable in this temperature range.

At ~ 80K, as shown in Fig. 2(c), the c(4x2) structure covers the surface. The structure of the complete p(2x2) arrangement is unstable at this temperature. A similar characteristic property to that obtained at 80K was observed on the surface at 30K. The structure of the c(4x2) observed at 30K is shown in Fig. 2(d). This indicates that the c(4x2) structure is the most stable even at 30K. As was previously shown, type P defects exist on the surface, and when the surface is perturbed, migration of the type P defects is initiated causing a reduction in the area of the p(2x2) arrangement [4].

At 6K, domains with the complete p(2x2) structure reemerged on the surface. Figure 2(e) shows an example of the STM image obtained at ~6K, in which c(4x2) and p(2x2) structures coexist together, and fluctuation between the two structures was observed. The phase transition between c(4x2) and p(2x2) structures is explained by the characteristic property of the type P defect which is formed on dimer rows. Namely, type P defect has a structure similar to that of the type C defect, that is, it consists of two adjacent dimers which are buckled with the same orientation. In addition, since they produce a phase shift, migration of the type P defect caused by the dimer flip-flop motion at the phase boundaries on dimer rows induces the apparent phase transition between the c(4x2) and p(2x2) arrangements (Fig. 2(d)). When the phase defect at the boundary migrates rapidly compared to the time scale of the STM measurement, it results in the symmetric imaging of dimers in the STM measurements [5].

Next let us consider the characteristic property of the type P defect using the Ising model. Figure 3 shows schematic diagrams of the arrangement of asymmetric dimers represented by Ising spins. In general, the tilt angle of the buckled dimers is assumed to take only two values, θ_0 and - θ_0. Therefore, thermal motion of the dimers induces flip-flop motion between the two angles. The absolute values of the coupling constants determined by Inoue et al. are V=51.9 meV. H=6.6 meV, and D=3.6 meV [20]. When a type P defect exists, a structure with parallel spin is introduced. In this case the coupling constant V is modified and becomes equal to G, of about 40 meV [21]. Here the definition and value of each interaction is taken from Inoue et al.

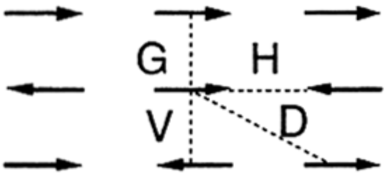

Fig. 3 Schematic of the Ising spin model and coupling constants defined in terms of V, G, H, and D.

Interaction between dimers obtained by Inoue et al. is highly anisotropic. Strong correlation along dimer rows even at room temperature was actually confirmed by the LEED measurements [15]. The characteristic property corresponds to our STM observation at 200K. A similar characteristic was also observed at ~ 6K; c(4x2) structural domains are formed as one-dimensional rather than twodimensional structures. These results indicate that interaction between dimers is stronger along dimer rows than that between adjacent dimer rows.

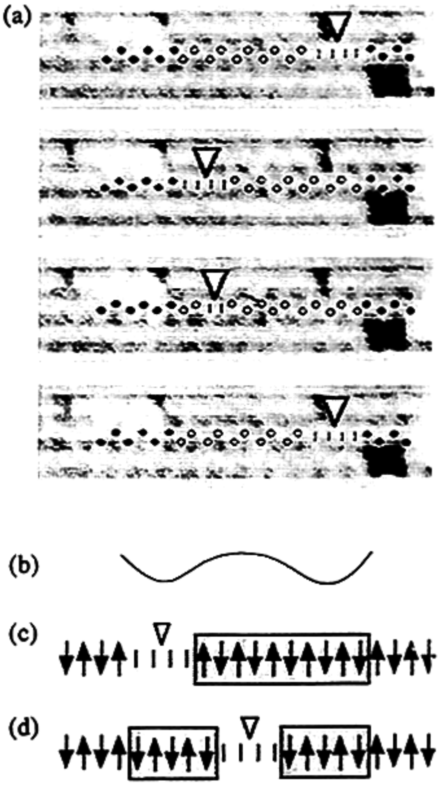

Fig. 4 (a) STM images of Si(100) surface continuously obtained at 200K. (b) A potential model for the type P defect in (a). Schematics of the Ising spin model for two cases in which a type P defect exists around (c) the side, and (d) central area of the domain.

Figure 4(a) shows a series of STM images taken at 200K (Vs=-2.0V, It=1.0nA), where a symmetric dimer region exists on a dimer row sandwiched between two buckled dimer regions. By comparing the phase of the buckled dimers on either side of the symmetric dimer area, we see that there is one type P defect in the symmetric dimer region. The symmetric dimer region changes its position according to the migration of the type P defect, but is located only around the sides of the dimer domain, and never appears in the central part. The observed results suggest the potential shape shown in Fig. 4(b) for the type P defect, as a function of its position along the dimer row. For analysis purposes, the schematics of an Ising spin model for the two cases in which a type P defect exists around the side and central area of the domain are shown in Figs. 4(c) and 4(d), respectively. Only when the nearest-neighbor interaction along the dimer row is considered, does the interaction energy of the 10 asymmetric dimers in the domain shown in Figs. 4(c) and 4(d) become the same: (c) $H_{10}=-10V$ and (d) $2H_5=-10V$. Here, V is the attractive interaction energy between two dimers, and H_n means the sum of the interaction energies of n asymmetric dimers. However, the observed phenomenon ($H_{10}<2H_5$) is different from the calculated result, and suggests the existence of a longer range interaction, which may also agree with the tendency of the 2x ordering of the dimer arrangement.

From 144K [16] to 30K, a complete c(4x2) structure was observed on the surface, indicating the strong interaction between dimer rows. In fact, when the surface is perturbed, the c(4x2) structure recovers by the dynamics of the type P defects; type P defects rearrange their locations to increase the area of the c(4x2) structure. Figure 5 shows an example of the structural change induced by the destruction of a type C defect at 80K (Vs=-0.6V, It=1.0nA). Since type C defect produce a phase shift, a p(2x2) arrangement exists on the left of the type C defect indicated by an arrow in Fig. 5(a). In order to study the interaction between dimer rows, the type C defect was removed by applying a voltage using the STM tip. As is shown clearly, the p(2x2) domain in Fig. 5(a) changed into the c(4x2) arrangement in Fig. 5(b). The observed change is explained by the creation and movement of the type

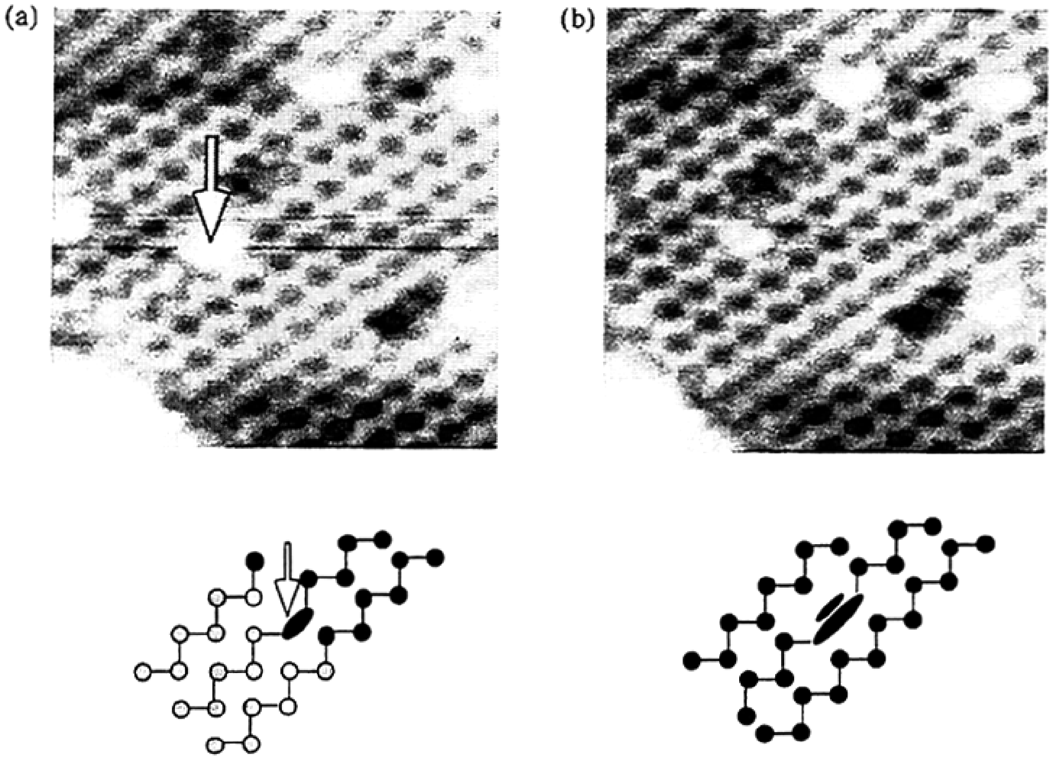

Fig. 5 STM images taken at 80K (a) before and (b) after destruction of the type C defect indicated by an arrow in (a).

P defect on the dimer row by the destruction of the type C defect. The observed results directly indicate the strong interaction between dimer rows and stability of the c(4x2) arrangement compared to that of the p(2x2) arrangement at this temperature.

Down to 30K, the p(2x2) domain formed on one side of the type C defect was unstable but it stabilized when the temperature was decreased to 6K. Let us discuss the observed structural change from 30K to 6K. The structure of the p(2x2) arrangement reemerges at 6K. A possible explanation is to relate the observed structural change to the coherent length of the correlation of dimer arrangement along dimer rows. When the correlation becomes stronger at lower temperatures, correlation between dimer rows may become weaker. However, as is well known, the order-disorder transition temperature is around 200K. Another explanation is to consider the change in the interaction between dimers. Since interaction energies of a dimer in c(4x2) and p(2x2) arrangements are -2V+2H-4D and -2V-2H+4D, respectively, change in the H/D ratio may cause the observed surface structural change.

In conclusion, phase of the buckled dimers was found to be strategically related to the atomic defects on the Si(100) surface. Since buckled dimers are frozen at low temperatures, the phase effect becomes more dominant at low temperatures. From the analysis of the temperature dependent dynamics of the type P defect, interaction between dimers was shown directly.

This work was supported by the Shigekawa Project of TARA, University of Tsukuba. The support of a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan is also acknowledged.

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