Streak patterns in low-energy electron diffraction on Si(001)

Masakazu Kubota* and Yoshitada Murata
Institute for Solid State Physics, The University of Tokyo, 7-22-1 Roppongi, Minato-ku, Tokyo 106, Japan
(Received 22 May 1992; revised manuscript received 23 November 1992)

The phase transition of Si(001) has been studied by investigating the temperature dependence of streak patterns in low-energy electron diffraction above the transition temperature. The streak pattern remains up to well above the transition temperature of $c(4\times2)$ to 2×1. The temperature dependence of the width and the length of the streak cannot be described by a simple two-dimensional Ising system. The result is discussed in terms of effects of a strong anisotropic coupling between adjacent asymmetric dimers, dimer vacancies, and a small amount of the $p(2\times2)$ configuration.

I. INTRODUCTION

The clean Si(001) surface is one of the simplest reconstructed surfaces. It consists of rows of dimers which are observed by scanning tunneling microscopy[1] (STM) and shows a phase transition between a 2×1 structure at room temperature and a $c(4\times2)$ structure at low temperatures.[2] This phase transition occurs around 200 K and can be represented by a second-order order-disorder transition. The appearance of the $c(4\times2)$ structure implies that the Si(001) surface is described by an asymmetric configuration of the dimers, since there is no possibility that a symmetric configuration shows a clear $c(4\times2)$ LEED pattern. This phase transition was theoretically predicted by Ihm *et al.*[3] and simulated using a Monte Carlo method by Saxena *et al.*[4] on the basis of an asymmetric dimer model represented by the Ising system, its stable configuration being the $p(2\times2)$ structure.

However, the asymmetric dimer model for the stable configuration is challenged by the STM measurements. At room temperature, a symmetric dimer arrangement is seen in the clean parts of the surface, the asymmetric configuration being restricted to the vicinity of dimer vacancies.[1,5] Then, a recent calculation including spin correlation claimed that the symmetric configuration of the dimers is more stable than the asymmetric one.[6] Detailed observations of the phase transition are expected to give important information for solving the problem of whether the dimers on Si(001) are asymmetric or symmetric.

Recent developments in surface physics make it possible to study two-dimensional critical phenomena such as order-disorder transitions on clean reconstructed surfaces and chemisorbed overlayers by using LEED.[7,8] In phase transitions, streak patterns play a significant role and are closely correlated with short-range ordering during the order-disorder transition. A streak pattern was observed on the Si(001)-2×1 surface[2] and also on the Ge(001)-2×1 surface.[9,10] In the present paper, we present precise measurements of the streak patterns correlated with the $c(4\times2)$ structure on clean Si(001) up to temperatures well above the transition temperature. The asymmetric configuration for the dimers is corroborated by the temperature dependence of the streak pattern in LEED.

II. EXPERIMENTS AND RESULTS

The experiments were performed using the same apparatus as described in previous papers.[2,11] A commercial mirror-polished wafer of Si(001) (p-type, 10 Ω cm) was washed in acetone or alcohol. The sample was held by a couple of tantalum electrodes. In an ultrahigh-vacuum chamber, the sample wafer was heated very slowly by passing a direct current through it and the temperature was held at 1500 K for 12 h. The sample was heated up to 1000 K for 10 s immediately before the measurements. A clean surface with very low defect density was reproducibly obtained. The amount of dimer vacancies was estimated to be less than a few percent of the surface atoms from the STM image.[12]

A video-LEED system equipped with a Varian fourfold LEED optics was used. A video camera using a silicon intensifier target (SIT) tube (Hamamatsu, C1000-12) was applied, because the SIT tube has high sensitivity and good linearity in the intensity measurements. LEED patterns were analyzed by using an image processing system. Each frame was divided into 512×512 sections and each section had a dynamic range of 8 bits. The intensity of the streak pattern is very weak as compared with that of the diffraction spots. A good signal-to-noise ratio was obtained by accumulating 256 pictures. However, the intensity in the very weak region showed a steplike change, because each address in the frame memory had only 8 bits, or 256 intensity levels.

Figure 1 shows a part of the contour of the LEED pattern. The incident energy E_p was 36 eV, and the specimen temperature was 350 K, which is well above the transition temperature. The upper left and lower right diffraction spots are half-order spots of (1 1/2) and (1/2 1), respectively. Clear streaks extend along the $\langle110\rangle$ directions through the half-order spots. Quarter-order spots appear at the middle points of the streaks with decreasing temperature. This pattern was observed from the double-domain surface. The sharp streak pattern shows that there exists long-range ordering in the dimer row and only short-range ordering in the direction perpendicular to the dimer row.

Figure 2 shows the temperature dependence of the LEED pattern in the top-view diagrams, which show the

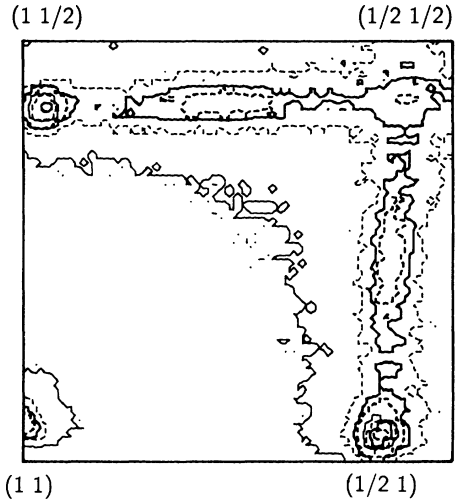


FIG. 1. Contour of a streak pattern in LEED on Si(001) at 350 K. $E_p = 36$ eV.

same region as that in Fig. 1. The electron energy was 36 eV. Weak streaks are observed at 450 K, which gain intensity when the temperature is decreased to 400 K. A weak and diffuse (1/2 1/2) spot characteristic to the $p(2\times2)$ structure is observed below 400 K at constant intensity, as shown at the top of each picture of Fig. 2. Quarter-order spots showing the long-range order appear

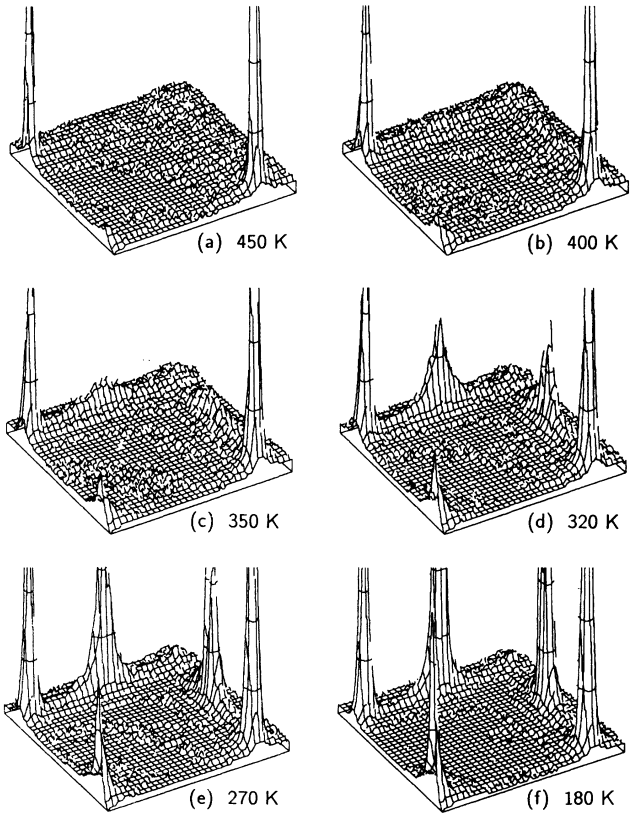
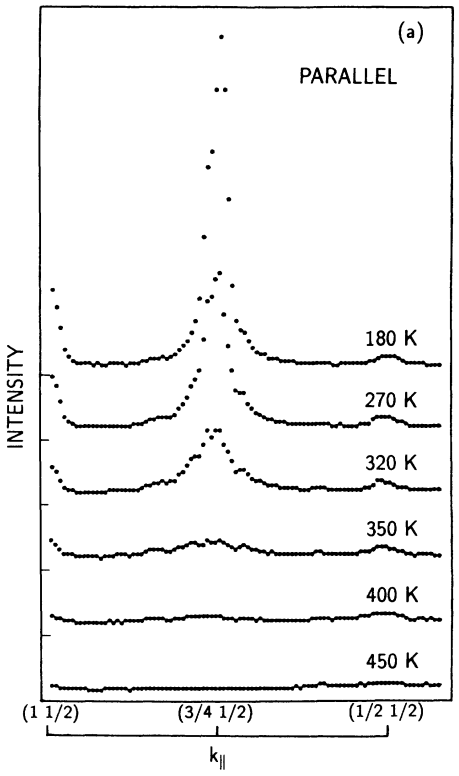


FIG. 2. Top view of LEED patterns on Si(001) as a function of specimen temperature. $E_p = 36$ eV. The intensity map observed in the same region as that in Fig. 1.



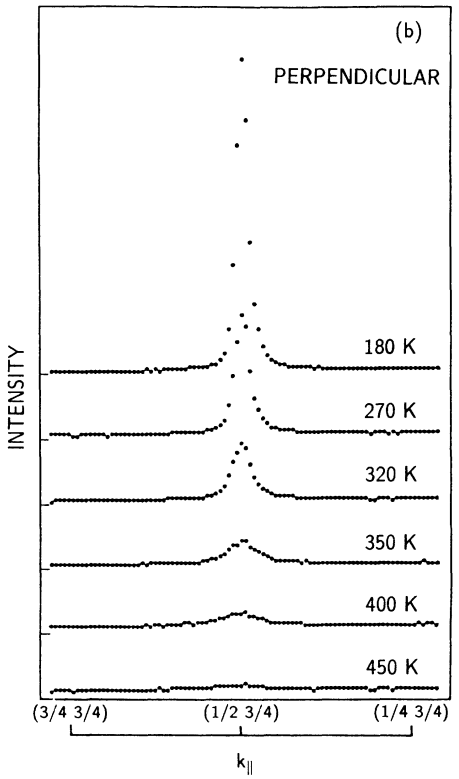


FIG. 3. Temperature dependence of intensity profiles for the streak on the Si(001) surface in the temperature range from 180 to 450 K. (a) Profiles parallel to the streak of the (3/4 1/2) spot and (b) perpendicular to the streak of the (1/2 3/4) spot. $E_p = 36$ eV.

clearly at 350 K and are strongly enhanced below about 270 K. A clear $c(4\times2)$ LEED pattern can be observed at 200 K.

In order to discuss the behavior of the streak patterns, the scattering profiles were analyzed. Figure 3(a) shows the intensity profiles parallel to the streak around the (3/4 1/2) spot and Fig. 3(b) shows those perpendicular to the streak around the (1/2 3/4) spot, which were observed over the temperature range from 180 to 450 K. The width and the length of the streak hardly change over the temperature range, at which the streak is clearly seen. This result is definitely shown by decomposing the intensity profiles with a Gaussian and a Lorentzian. Figure 4 demonstrates fitting with a Gaussian and a Lorentzian for the intensity profiles parallel and perpendicular to the streak around the quarter-order spot observed at 270 K. The Gaussian corresponds to the diffraction spot, which represents the long-range ordering, and the Lorentzian gives a streak pattern the length of which shows the short-range ordering.

Figure 5 shows the result deduced from the decomposition of the intensity profiles shown in Fig. 3 as a function of temperature. The widths of the spot perpendicular and parallel to the streak show the same tendency. The length of the streak remains constant, while the width of the streak remains nearly constant and above 300 K increases gradually with increasing temperature. The height of the streak also remains constant up to 300 K, then decreases gradually. The width of the quarter-order diffraction spot increases with increasing temperature.

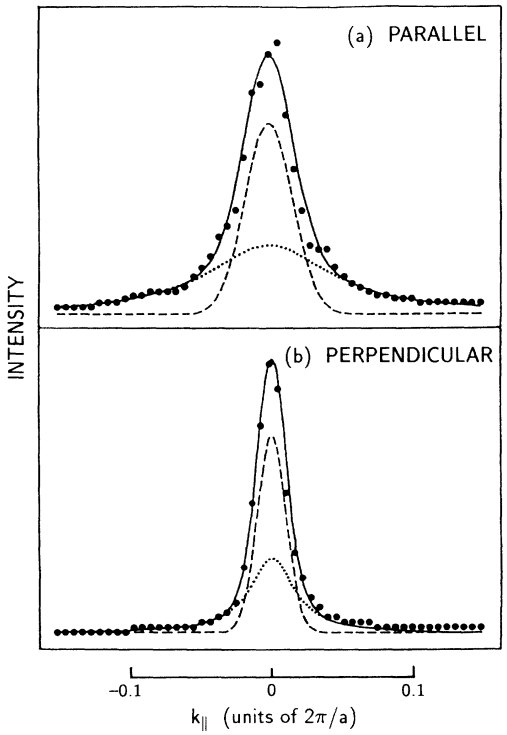


FIG. 4. Decomposition of the intensity profile observed at 270 K (closed circles) by using a Lorentzian (dotted curve) and a Gaussian (broken curve). Solid line shows the fitting curve, which is the sum of the Lorentzian and the Gaussian.

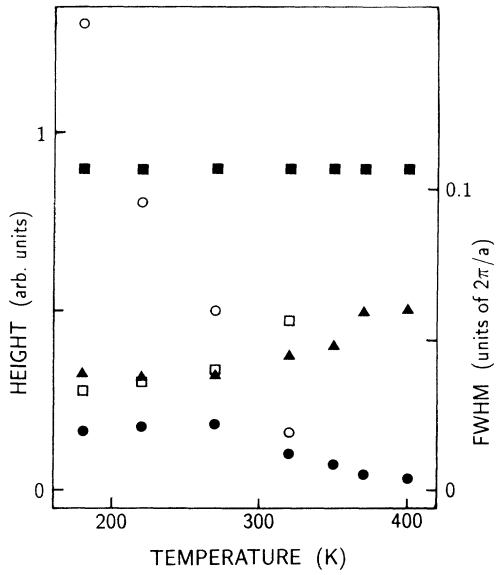


FIG. 5. Temperature dependence of the width (closed triangle), the length (closed square), and the height (closed circle) of the streak, and the width (open square) and the height (open circle) of the (3/4 1/2) spot, which were obtained by decomposition of the observed intensity profile.

III. DISCUSSION

The length of the streak remains constant and the height and the width of the streak hardly change over the entire temperature range, as shown in Figs. 3 and 5. This result is clearly different from that derived from a simple two-dimensional Ising system, as described below.

Dynamical diffraction effect can be ignored when analyzing the intensities of the streak pattern, because the streak pattern shows the same behavior at various primary energies of the incident electrons. This property of the streak pattern in the case of silicon in particular is due to little multiple scattering.[13] Hence, one can analyze the streak pattern with the kinematic diffraction scheme concerning only the topmost atomic layer in order to discuss the phase transition. In the kinematic limit, the LEED intensity is the Fourier transform of the two-site correlation function. The Fourier transforms of the pair correlation function give a Lorentzian representing a diffuse and/or streak pattern and a Gaussian representing a diffraction spot. Therefore, short-range ordering can be taken account of by fitting the observed profiles with a superposition of a Gaussian and a Lorentzian. The Lorentzian gives the streak pattern in the present case. The critical exponents, ν and γ, of the usual two-dimensional system can be determined from the Lorentzian measured as a function of temperature around the transition temperature, T_c. The width of the Lorentzian is given by $|1-T/T_c|^{\gamma}$.[7,8] Around T_c, the streak pattern converges on the diffraction spot with decreasing temperature.

The present experimental result shows that the width of the Lorentzian parallel to the streak, i.e., the length of the streak, remains constant in a wide temperature

range and the width perpendicular to the streak increases slightly above 300 K, as seen in Fig. 5. This result is clearly different from that derived from the simple two-dimensional Ising system. Moreover, the intensity-versus-temperature curve for a quarter-order spot[2] is also impossible to be represented by the usual system, because the observed curve deviates from Onsager's thermodynamic formula,[14] as shown in Fig. 6. Onsager's thermodynamic formula shows a sharp change of the intensity just below the critical temperature, but in the present system the intensity changes sigmoidally. These experimental results will be discussed with the help of a few modifications to the simple two-dimensional Ising system.

At first, we shall consider the strongly anisotropic coupling between the adjacent dimers. The streak pattern appears when the coupling within the dimer row is much stronger than that between dimer rows. This strong coupling may be explained by adding the effect of a displacement of the second-layer atoms. The buckling arrangement of antiferromagnetic ordering could be more stabilized by an alternating displacement of the second-layer atoms along the dimer row, as shown by arrows in Fig. 7(a), where the Si-Si backbond distance remains constant. On the other hand, a displacement of the second-layer atoms without any change of the Si-Si backbond length is hard to imagine in the case of ferromagnetic ordering. A similar argument has been discussed for the Ge(001) surface.[15]

A strongly anisotropic two-dimensional phase transition is clearly at variance with the result of the Monte Carlo simulation by Saxena *et al.*,[4] which shows an isotropically randomized system. In this simulation the coupling constants derived from the tight-binding approximation were used, i.e., $H/V=-0.38$ and $D/V=-0.15$, with the coupling constants for the spin Hamiltonian, V, H, and D, as shown in Fig. 8. These values are given by considering the classical dipole-dipole interaction.[16] A much smaller value of $|H/V|$ is obtained by adding the effect of the second-layer displacement.

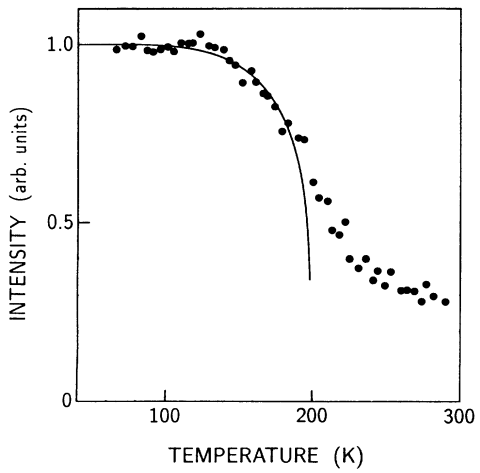


FIG. 6. Temperature dependence of the intensity of the (3/2 3/4) spot with the Debye-Waller correction. Solid line represents the curve according to Onsager's formula.

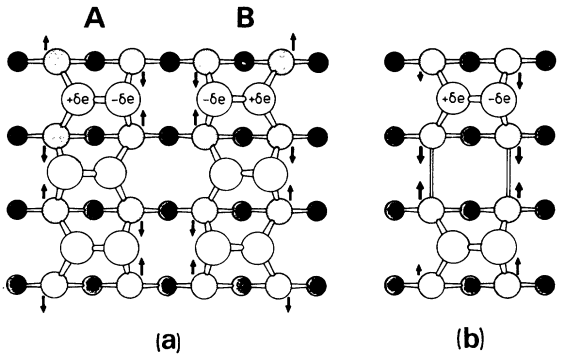


FIG. 7. Top view of the Si(001) surface of (a) the clean $c(4\times2)$ surface and (b) the surface with a dimer vacancy. Larger (smaller) open circles indicated by $-\delta e(+\delta e)$ show upper (lower) atoms constructing the dimer. The arrows show the displacement vector of the second-layer atoms for the stabilized arrangement of the buckling configuration.

The streak pattern seen in the experiment slightly above the transition temperature can be reproduced by using $H/V \sim -0.05$ in a Monte Carlo simulation.[17,18] However, the simulated streak length decreases with increasing temperature, which is contradictory to the observed result. The observed result shows that the streak length remains constant. That is, this model does not reproduce the present experimental results.

Next, we shall discuss the effect of vacancies. On the Si(001) surface, dimer vacancies are spontaneously produced and a special technique is necessary for reducing them. Even small amounts of random dimer vacancies affect the phase transition.[19] The tail appearing in the temperature dependence of the intensity of the quarter-order spot is considered to be due to the influence of random vacancies. In fact, a Si(001) surface containing a higher density of dimer vacancies shows no phase transition.[20] Dimer vacancies can reduce the number of dangling bonds and lower the electronic energy. The elastic strain energy increases due to the distortion field connected with the dimer vacancy formation, as shown in Fig. 7(b). This distortion field freezes the flip-flop transformation of the asymmetric dimer within a dimer row but not in the direction perpendicular to the dimer row. Hence, areas for the in-phase transformation in the flip-flop motion are limitted with finite size, which is divided by the domain walls connected to dimer vacancies. The sigmoidal shape seen in Fig. 6 reflects finite size effects of the domain.[21]

A domain wall forms the $p(2\times2)$ configuration. We designate elements of the antiferromagnetic ordering in

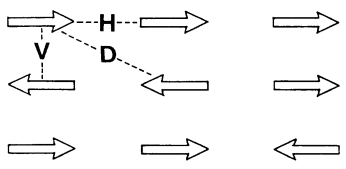


FIG. 8. Coupling constants used in the spin Hamiltonian, V, H, and D. Asymmetric dimer configuration of the Si(001) surface is schematically illustrated by arrows.

the dimer row as A and B marked in Fig. 7(a). Then, ordering of $ABAB\cdots$ and $AAAA\cdots$ give $c(4\times2)$ and $p(2\times2)$, respectively. If the flip-flop transformation occurs between the A and B configuration in each domain, the structure changes between $ABABAABAB$ and $BABAB\mathbf{A}ABA$, in which **A** is connected with a dimer vacancy.

Thus the $p(2\times2)$ configuration is partially formed. This consideration is supported by the facts that a weak and diffuse (1/2 1/2) spot characteristic to the $p(2\times2)$ structure was observed below 400 K at constant intensity, as seen in Fig. 2, and that the $p(2\times2)$ structure can be observed in the STM image of Si(001) at low temperature.[22]

In conclusion, the temperature dependence of the streak patterns observed on the Si(001) surface can be interpreted by the strongly anisotropic two-dimensional Ising system, in which the ground-state configuration is $c(4\times2)$, with a small amount of the asymmetric dimers in the $p(2\times2)$ configuration. Small amounts of dimer vacancies may also affect the phase transition.

ACKNOWLEDGMENTS

We are grateful to Professor A. Yoshimori and Professor K. Terakura for helpful discussions. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

* Present address: Department of Electronics, The Polytechnic University, 4-1-1, Hashimoto-dai, Sagamihara, Kanagawa 229, Japan.

[1] R. M. Tromp, R. J. Hamers, and J. E. Demuth, Phys. Rev. Lett. **55**, 1303 (1985).
[2] T. Tabata, T. Aruga, and Y. Murata, Surf. Sci. **179**, L63 (1987).
[3] J. Ihm, D. H. Lee, J. D. Joannopoulos, and J. J. Xiong, Phys. Rev. Lett. **51**, 1872 (1982).
[4] A. Saxena, E. T. Gawlinski, and J. D. Gunton, Surf. Sci. **160**, 618 (1985).
[5] R. J. Hamers, Ph. Avouris, and F. Bozso, Phys. Rev. Lett. **59**, 2071 (1987).
[6] E. Artacho and F. Yanduráin, Phys. Rev. Lett. **62**, 2491 (1989); E. Artacho and F. Yanduráin, Phys. Rev. B **42**, 11 310 (1990).
[7] R. F. Willis, in *Dynamical Phenomena at Surfaces, Interfaces and Superlattices*, edited by F. Nizzoli, K.-H. Rieder, and R. F. Willis (Springer, Berlin, 1985), p. 126.
[8] T. L. Einstein, in *Chemistry and Physics of Solid Surfaces VII*, edited by R. Vanselow and R. Howe (Springer, Berlin, 1988), p. 307.
[9] S. D. Kevan, Phys. Rev. B **32**, 2344 (1985).
[10] R. J. Culbertson, Y. Kuk, and L. C. Feldman, Surf. Sci. **167**, 127 (1986).
[11] Y. Murata, H. Tochihara, and M. Kubota, in *Metallization and Metal-Semiconductor Interfaces*, edited by I. P. Batra (Plenum, New York, 1989), p. 367.
[12] T. Hashizume, Y. Hasegawa, I. Kamiya, T. Ide, I. Sumita, S. Hyodo, T. Sakurai, H. Tochihara, M. Kubota, and Y. Murata, J. Vac. Sci. Technol. A **8**, 233 (1990).
[13] M. A. Van Hove, W. H. Weinberg, and C.-M. Chan, *Low-Energy Electron Diffraction* (Springer, Berlin, 1986).
[14] L. Onsager, Phys. Rev. **65**, 117 (1944); C. N. Yang, *ibid.* **85**, 808 (1952); C. H. Chang, *ibid.* **88**, 1422 (1952); E. W. Montroll, R. B. Potts, and J. C. Ward, J. Math. Phys. **4**, 308 (1963).
[15] M. C. Payne, M. Needels, and J. D. Joannopoulos, J. Phys. Condens. Matter **1**, SB63 (1989).
[16] Y. Murata, M. Kubota, and T. Tabata, in *Ordering at Surfaces and Interfaces*, edited by A. Yoshimori and T. Shinjo (Springer, Berlin, 1992), p. 93.
[17] K. Kakitani and A. Yoshimori, in *Ordering at Surfaces and Interfaces*, edited by A. Yoshimori and T. Shinjo (Springer, Berlin, 1992), p. 137.
[18] M. Kubota, N. V. Richardson, and Y. Murata (unpublished).
[19] Y. Imry and S.-K. Ma, Phys. Rev. Lett. **35**, 1399 (1975).
[20] T. Aruga and Y. Murata, Phys. Rev. B **34**, 5654 (1986).
[21] D. P. Landau, Phys. Rev. B **13**, 2997 (1976).
[22] R. A. Wolkow, Phys. Rev. Lett. **68**, 2636 (1992).

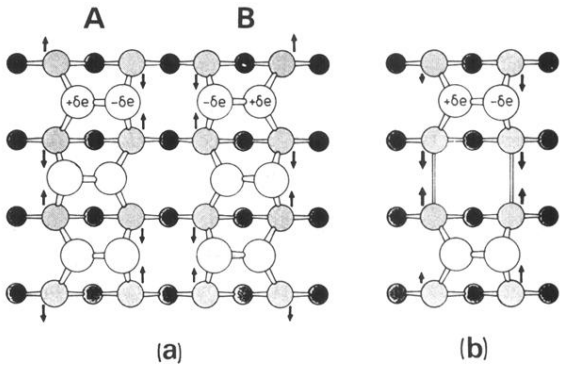


FIG. 7. Top view of the Si(001) surface of (a) the clean $c(4\times2)$ surface and (b) the surface with a dimer vacancy. Larger (smaller) open circles indicated by $-\delta e(+\delta e)$ show upper (lower) atoms constructing the dimer. The arrows show the displacement vector of the second-layer atoms for the stabilized arrangement of the buckling configuration.