Field-induced instability of dimer structures near single-layered steps on Si(001) surfaces

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Abstract. We study the structural stability of single-layered steps on Si(001) 2×1 surfaces where the static electric field is applied in the [110] direction, using a one-dimensional tight-binding model which takes account of dimer-bond and dangling-bond states of this surface. When the electric field exceeds a critical value, the dimer structures near the step edges are substantially weakened via creation of the soliton-like states. The two-band nature of the surface states induces asymmetry of the instability of the step edges depending on the direction of the field. Based on our results, we discuss the recent experimental observation of the switching of the $(2 \times 1)/(1 \times 2)$ domains of single-layered vicinal Si(001) surfaces during heating with direct current.

1. Introduction

Investigation of geometric structures of Si(001) 2×1 vicinal surfaces has been a subject of interest. It is well known [1] that the structures of the single-layered steps on Si(001) surfaces are classified into two types: S_A and S_B. The dimer rows on the upper terrace of S_A and S_B steps run perpendicular and parallel to the step edges, respectively (see figure 1(a)). As for the electronic structures of the steps, however, there have been few studies [2]. We note that the structure of the 2×1-reconstructed Si(001) surface is strongly anisotropic. This anisotropy affects electronic structures as well as elastic properties of this surface.

Recently, conversions of the major domains on Si(001) vicinal surfaces with single-layered steps have been observed during heating by direct electric current. Latyshev *et al* [3] found, using reflection-electron-microscope imaging of the surface misoriented toward the [110] direction, that the (1×2) domains dominate the others when the electric current flows in the step-down direction and that the major domains switch when the current flows in the step-up direction. This was observed above 1200 K. They suggested that surface atoms are charged up to migrate on the surface under the current (*electromigration* of silicon atoms) and that anisotropy of the surface diffusion should be responsible for the domain conversion. Ichikawa and Doi [4] found that, when the sample is heated above 900 K, either the S_A or the S_B step becomes less stable than the other, depending on the direction of the electric current used for

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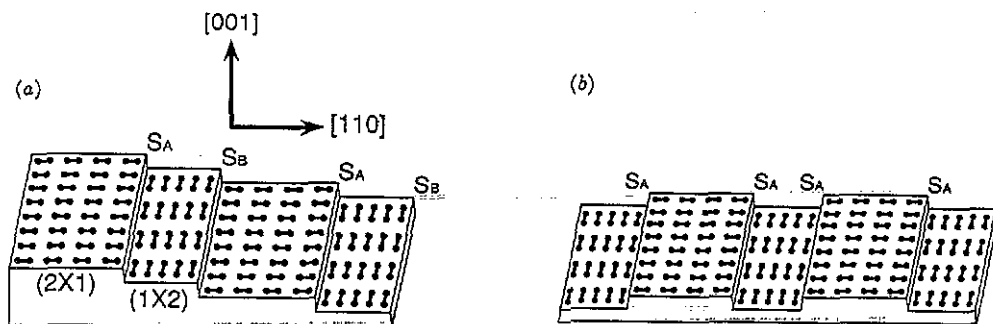
Figure 1. Schematic diagrams of the single-layered Si(001) 2 × 1 surface. (*a*) The vicinal surface with alteration of S_A and S_B steps. (*b*) Stripes bounded by S_A steps.

heating. Kahata and Yagi [5] found that the terrace width of a minor domain does not decrease below some critical value. Stoyanov [6] first challenged this problem in a theoretical way. He proposed a kinetic model of surface diffusion on Si(001) and calculated the magnitude of the force which acts on silicon adatoms to migrate. Natori *et al* [7] developed the kinetic model of Stoyanov and took account of the repulsive interactions between steps in order to explain the critical terrace width of the minor domans.

The purpose of this paper is to investigate the structural stability of single-layered steps on a Si(001) surface under static electric fields in the [110] direction. From the viewpoint of *electronic structures* of the steps, we seek the possibility of asymmetry of the field-induced instability of the steps depending on the direction of the field. For this purpose we propose a simple tight-binding model of the Si(001) surface where we take account of two bands characteristic of this surface. The major point of interest is to investigate how the relative positions of the two bands affect the stability of the steps under the fields.

2. The two-band model

From the first-principles electronic-structure calculations in the local-density-functional approximation (LDA) [8], it is believed that the electronic structure of the Si(001) 2 × 1 surface is characterized by two surface states: σ-band and π-band. The energy gain by (2 × 1) reconstruction (approximately equal to 1.8 eV per dimer) is mainly due to a large energy gap of the σ-band (approximately 1.5 eV). It is important to note that the direction of the dimerization differs layer by layer because of the anisotropic geometry of this surface. This means that a mixture of domains of dimers with different dimerization directions does not occur on a same atomic plane. Thus the strong anisotropy of the surface structure imposes restrictions on the direction of easy hopping of electrons. The π-band determines whether the surface is semiconducting or metallic. Recent calculations by Inoue *et al* [9] have shown that this surface is semiconducting with the indirect energy gap of 0.23 eV when is reconstructed by the c(4 × 2) symmetry.

Bearing in mind the above, we shall construct a tight-binding model of a Si(001) surface as an electron–phonon system. We consider two bands which correspond to π- and σ-bands. Since the dimer reconstruction of this surface can be viewed as the

Peierls transition, we use the Su–Schriefer–Heeger (SSH) form of the electron–phonon interaction [10]. We consider a 'striped' structure (see figure 1(*b*)), which has *only* S_A steps, instead of the usual 'staircased' one as shown in figure 1(*a*). The use of this structure is motivated by the theoretical prediction that the Si(001) surface at very low temperatures should have the repeated stripes bounded by S_A steps [11]. To the first approximation, we can regard a stepped surface as a one-dimensional system whose coordinate axis runs perpendicular to the step edges. This is a chain of dimers stretched in the direction of a dimer-bond axis. We note that the chain has a finite length. We describe a step as a simple truncation of the chain with free boundaries. Nearest-neighbour electron hoppings along the chain are taken into account. We consider the bending distortion of backbonds in the harmonic approximation. Finiteness of the chain means that electrons are confined within the chain. Since electrons would actually be allowed to cross the steps between upper and lower terraces, our model seems too simple. As mentioned above, however, Si(001) 2 × 1 surfaces have a strong anisotropy of the overlapping of the orbitals because the direction of dimerization rotates by 90° terrace by terrace (see figures 1(*a*) and (*b*)) in the case of single-layered steps. Therefore transfer of the electrons across the steps would be much smaller than that inside the terraces. Since we are interested in changes in the electron distribution and the dimer structures caused by the electric field applied in the direction *parallel* to the chain, the effect of π interaction between the chains (or equivalently, *perpendicular* to the chain) on those properties should be of minor importance. Thus the use of the one-dimensional finite change is justified as a first approximation.

The Hamiltonian of our one-dimensional two-band model is described as

$$\hat{H} = -\sum_{\lambda=\sigma,\pi}\sum_{n,s}[t_\lambda - \alpha_\lambda(u_n - u_{n-1})]\left(a_{n,s}^{(\lambda)\dagger}a_{n-1,s}^{(\lambda)} + a_{n-1,s}^{(\lambda)\dagger}a_{n,s}^{(\lambda)}\right) + \frac{K}{2}\sum_n u_n^2$$

$$+ \sum_{n,s}\Delta E a_{n,s}^{(\pi)\dagger}a_{n,s}^{(\pi)} + \sum_{n,s}(Fnl_0)\left(a_{n,s}^{(\sigma)\dagger}a_{n,s}^{(\sigma)} + a_{n,s}^{(\pi)\dagger}a_{n,s}^{(\pi)}\right) \qquad (1)$$

where $a_{n,s}^{(\lambda)}$ and $a_{n,s}^{(\lambda)\dagger}$ are annihilation and creation operators of an electron of an orbital λ with spin s at an nth atomic site, u_n a displacement of an atom at an nth site from its equilibrium position, t_λ and α_λ the hopping integrals between nearest-neighbour sites and the electron–phonon coupling constant, K the spring constant for the bending of a backbond, ΔE the difference in the positions of the energetic centres of mass of the σ-band and π-band, F the magnitude of the external electric field, and l_0 the lattice spacing, 3.84 Å, respectively.

We calculate the ground-state structures under various electric fields by optimizing the system with respect to both electronic and geometric degrees of freedom in the Born–Oppenheimer approximation. From the condition that the variation of the total energy with respect to the displacements should be zero, we obtain the simultaneous equations for the displacements:

$$u_n = -\frac{2}{K}\sum_{\lambda,s}\sum_{\nu\in\text{occ}}\alpha_\lambda\left\langle\nu\left|a_{n,s}^{(\lambda)\dagger}a_{n-1,s}^{(\lambda)}\right|\nu\right\rangle \qquad n = 1, 2, \ldots, N \qquad (2)$$

where $|\nu\rangle$ is the eigenvector of the Hamiltonian. Giving the initial values to the displacements, we solve these equations in a self-consistent way. The iteration process is continued until the criteria $\max\{(2\alpha_\sigma/t_\sigma)|u_n^{(i)} = u_n^{(i-1)}|\} \leqslant 10^{-5}$ is satisfied,

where $u_n^{(i)}$ is the displacement of the nth atom obtained in the ith iteration stage. In order to investigate the properties of the system, we calculate optical components of the displacements, charge densities and local densities of states (the LDOS). The optical components of the displacements are defined as

$$y_n^{\text{opt}} = \left[(-1)^{n-1}/2\right](u_n - u_{n-1}).$$ (3)

The amplitude of y_n^{opt} is the average displacement of the two atoms. Its sign is the 'phase' of the dimer bonding. For example, the sign of y_n^{opt} is positive if a dimer is composed of an atom at the even-number site displacing in the positive direction and the other in the negative direction. The LDOS is defined as

$$D_n(E) = \sum_\nu \delta(E - E_\nu)|\langle n|\nu\rangle|^2.$$ (4)

To analyse the eigenstates projected on each atomic site, we actually calculated the *number* of states defined as

$$N_\nu(n, m) \equiv \sum_{l=n}^{m} \int_{E_\nu - 0_+}^{E_\nu + 0_+} D_l(E)\,\mathrm{d}E = \sum_{l=n}^{m} |\langle l|\nu\rangle|^2.$$ (5)

The values of the parameters in the Hamiltonian are determined so that the *result with $F = 0$ reproduces the band width and energy gap of the surface states* obtained from the *ab initio* calculations [8]. Since the electronic states of the Si(001) 2×4 surface are anisotropic, care must be taken of the parametrization of the *one-dimensional* Hamiltonian. From the LDA results of the π-band structure we assume the width $4t_\pi$ and the indirect gap $E_g(\pi)$ to be 2 eV and 0.23 eV, respectively. The band structure of the σ-bond states is not clearly shown in existing literature. We assume that $4t_\sigma = 5$ eV and that the gap $E_g(\sigma)$ opened by dimerization is 1.5 eV. Since our parametrization is not intended to reproduce the precise geometry of the reconstructed surface, we neglect the asymmetry of the dimer structure. Thus, the displacement of each surface atom from its ideal position, u_0, was estimated to be 0.77 Å. From this value and the energy gaps of the two bands, the electron–phonon coupling constants α_π and α_σ were determined to be 0.0373 eV Å^{-1} and 0.2435 eV Å^{-1}, respectively. The spring constant K was found to be 14.576 eV Å^{-2}.

Although the value of ΔE is unknown, we chose the value of -0.375 eV from the band structure along the Γ–J line for the 2×1-reconstructed surface calculated by Kruger and Pollmann [8]. It is plausible to ascribe the physical origin of negative ΔE to the correlation effect of electrons. That is, the energy levels of the bonding orbitals can be raised because of the Coulomb repulsion between pairs of electrons accommodated in each level. Since the σ-electrons are more localized than the π-electrons, the Coulomb repulsion between the former is stronger than the latter. Thus the bonding σ-band is more lifted than the bonding π-band is, leading to negative ΔE.

3. Results and discussion

We calculated the ground-state structures systematically by varying the strength of the field. We refer to the field as $Fl_0 N$, where N is the cluster size, rather than F

itself. It is varied from 0 eV to 1.25 eV with an interval of 0.025 eV. Several initial conditions were tested to discard local minima. Calculations were performed using a cluster with $N = 100(384$ Å long).

When the field is zero, the optical component of the displacement is close to 0.77 Å inside the chain, as it should be (see figure 2(a)). It is enhanced near the chain ends up to 1.1 Å. This means that an atom on the edge is connected to only one neighbour, so the bond becomes stronger than in the bulk. The distributions of the π- and σ-electrons are exactly equal to one electron per site (see figure 2(b)). If the field is sufficiently weak, only the intra-dimer polarization occurs although it is so small that the optical component of the displacements and the charge distributions are essentially the same as in the zero-field case.
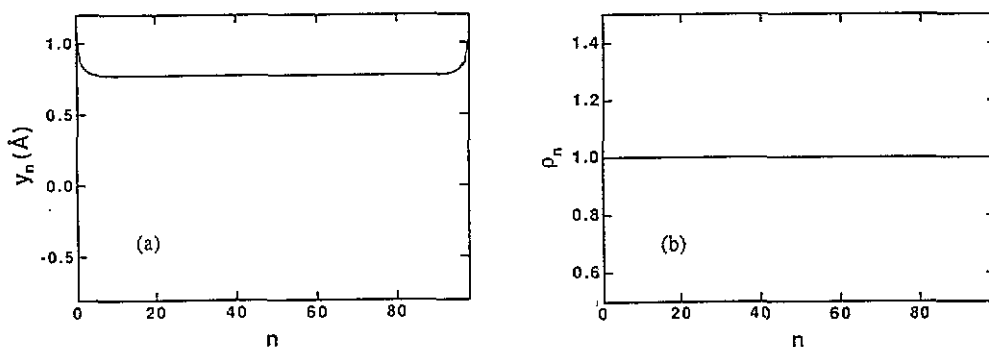

Figure 2. Lattice structure and charge distribution with $F l_0 N = 0$ eV. (a) The optical component of the displacement. (b) The charge distribution (electrons per site). It should be noted that both π- and σ-electrons are distributed with the same density, as they should be.

When the field becomes stronger than a threshold value, $F_c l_0 N > 0.35$ eV, both the lattice structure and charge distribution become strongly asymmetric as shown in figure 3. The optical component of the displacements in figure 3(a) has different structures on the intervals $[0, 49]$ and $[69, 98]$. It has two shallow minima, 0.68 Å at $n = 6$ and 0.71 Å at $n = 23$, respectively. In contrast, the optical component passes zero near $n = 83$ and 93, reaching a deep minimum in between, i.e., -0.58 Å at $n = 88$. This means that on the latter region the dimer bonds are substantially weakened and that the phase of the bonding is reversed at $n = 83$ and 93, respectively. In this sense we can call these structures domain walls, or *solitons*. We see from the charge distribution in figure 3(b) and numerical integration of the charge density that the number of π-electrons increases by four in the range $[0, 49]$ with no change of the number of σ-electrons, while both π- and σ-electrons decrease by two in the range $[69, 98]$ respectively, with respect to the case of $F = 0$.

We calculated the number of states which was defined in equation (5). In figures 4 and 5, $N_\nu(0,49)$ and $N_\nu(69,98)$ are shown for $F l_0 N = 0$ eV and 0.36 eV, respectively. Since the number of electrons integrated over the range $[0, 49]$ is just half of the total electron number when $F l_0 N = 0$ eV, $N_\nu(0, 49)$ is exactly equal to 0.5 irrespective of the value of ν for both bands, as shown in figure 4(a) (see appendix). From the distribution of intervals between the neighbouring bars, it is easy to see the cosine character of the two bands. As for $N_\nu(69, 98)$, which is shown in figure 4(b), the average height is equal to 0.3 (see appendix). The distribution of the local number of
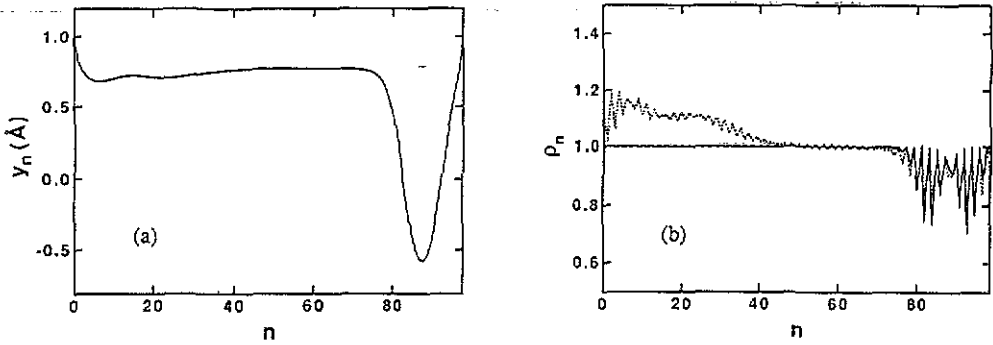
Figure 3. The same as figure 2 with $Fl_0 N = 0.36$ eV. In panel (b), the density of π-electrons is represented by a dashed line and of σ-electrons by a solid line, respectively.
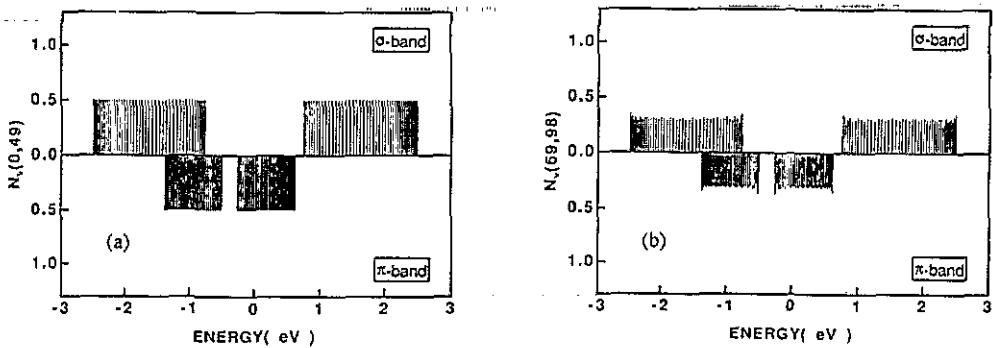

Figure 4. The number of site-projected eigenstates integrated over the ranges of (a) [0, 49] and (b) [69, 98], respectively, with $Fl_0 N = 0$ eV. The ranges of integrations are taken so as to enclose the solitons of the right-hand edge and the weak lattice distortions of the left-hand edge, which are shown in figure 5, with the smallest possible number of sites.

states with $Fl_0 N = 0.36$ eV is shown in figures 5(a) and (b). The chemical potential is chosen as the zero of the energy. Localized states appear in the energy gap of each band, which we label as S_1, S_2 for the σ-band, and P_1, P_2, P_3 and P_4 for the π-band, respectively. S_1 and S_2 states are located 0.354 eV and 0.515 eV, respectively. From the squared amplitudes of these states shown in figure 6(a), S_1 and S_2 are identified with the states of soliton pair originated from the σ-band on the right-hand edge of the chain. Since the number of both states integrated over the interval [69, 98] is unity (see figure 6(b)), these states are localized on this region and empty. The two states are formed as a result of the coupling of the two solitons. P_1 and P_2 states (see figure 6(a)) are located -0.004 eV and -0.063 eV and completely filled with electrons. They are donor-like states which stem from the bottom of the anti-bonding π-band. The soliton states derived from the π-band are labelled P_3 and P_4, which *are positioned 0.004 eV and 0.104 eV (see figure 6(c)).*

In order to consider the asymmetric soliton structure in terms of the electron filling, we show in figure 7 the schematic illustrations of π- and σ-bands near chain edges. The distribution of the energy levels of the chain edges is exactly the same without the field (see figure 7(a)). Figure 7(b) shows the situation under the field where four electrons are simply transferred from the bonding π-band of the right
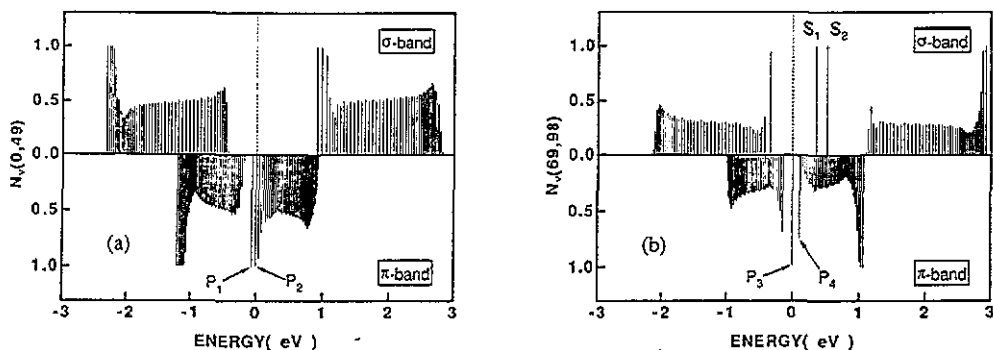
Figure 5. The same as figure 4, but with $Fl_0 N = 0.36$ eV. The position of the chemical potential, which is also specified by the dashed line, is chosen to be the zero of the energy. (*a*) Donor-like states P_1 and P_2 formed under the edge of the anti-bonding π-band. (*b*) Soliton states S_1 and S_2 are formed in the mid-gap of the σ-band, and P_3 and P_4 of the π-band, respectively.

edge to the anti-bonding π-band of the left edge of the chain. In figure 7(*b*), the top of the bonding π-band of the right edge is higher in energy by $\sim FN$ ($N = 100$ in the present case) relative to that of the left edge. Additionally, overlapping of the bonding and the anti-bonding p bands occurs. Therefore π-electrons are transferred to the bottom of the π^*-band and the system becomes metallic. As is already described, this occurs when the field is weak. However, this configuration becomes unstable against the formation of solitons when the field becomes stronger than a threshold. The energy levels are distributed as shown in figure 7(*c*) where the solitons are created asymmetrically. Whether the dimerized or the soliton structure is favoured is determined from the competition between the electronic and the geometric contribution to the energy lowering. If the energy gain by the relaxation of a lattice from the dimerized structure overcomes the energy loss due to excitation of π-electrons in the donor-like states, then the soliton structure is realized. The origin of the stabilization of the asymmetric soliton structure comes from the pairing of two solitons which produces a large region with relaxed backbonds.

We compare our results with the experimental observation of the current-induced conversion of the major domains on vicinal Si(001) 2×1 surfaces with single-layered steps. It has been argued [3–6] that instability of steps is caused by the thermal fluctuation and that switching of the major domains is due to current-induced mass transport whose velocity is modulated with anisotropy of the surface diffusion constants. However, thermal fluctuation is not the only cause of the domain conversion for the following reasons. First, the thermal fluctuation, as low as 0.1 eV, is far below the energy required to break covalent bonds to separate silicon atom from the step edge, $\simeq$ 4–5 eV, as suggested from the calculations of Yamaguchi and Fujima [2]. From our results, considerable reduction of the activation energy can be available via the formation of solitons which substantially weaken the dimer bonds. Excitation of kinks may be another possible mechanism to lower the bond breaking energy effectively. In order to make clear whether the kinks are essentially important as sources of adatoms, it may be necessary to calculate the energy barrier to the removal of an atom positioned at a kink site. Second, the instability of the step edges would be *independent* of the direction of the electric current because the random force due to thermal fluctuations is isotropic. Our results show that the large distortions of the dimers occur when the field is applied in the step-down direction. We note that
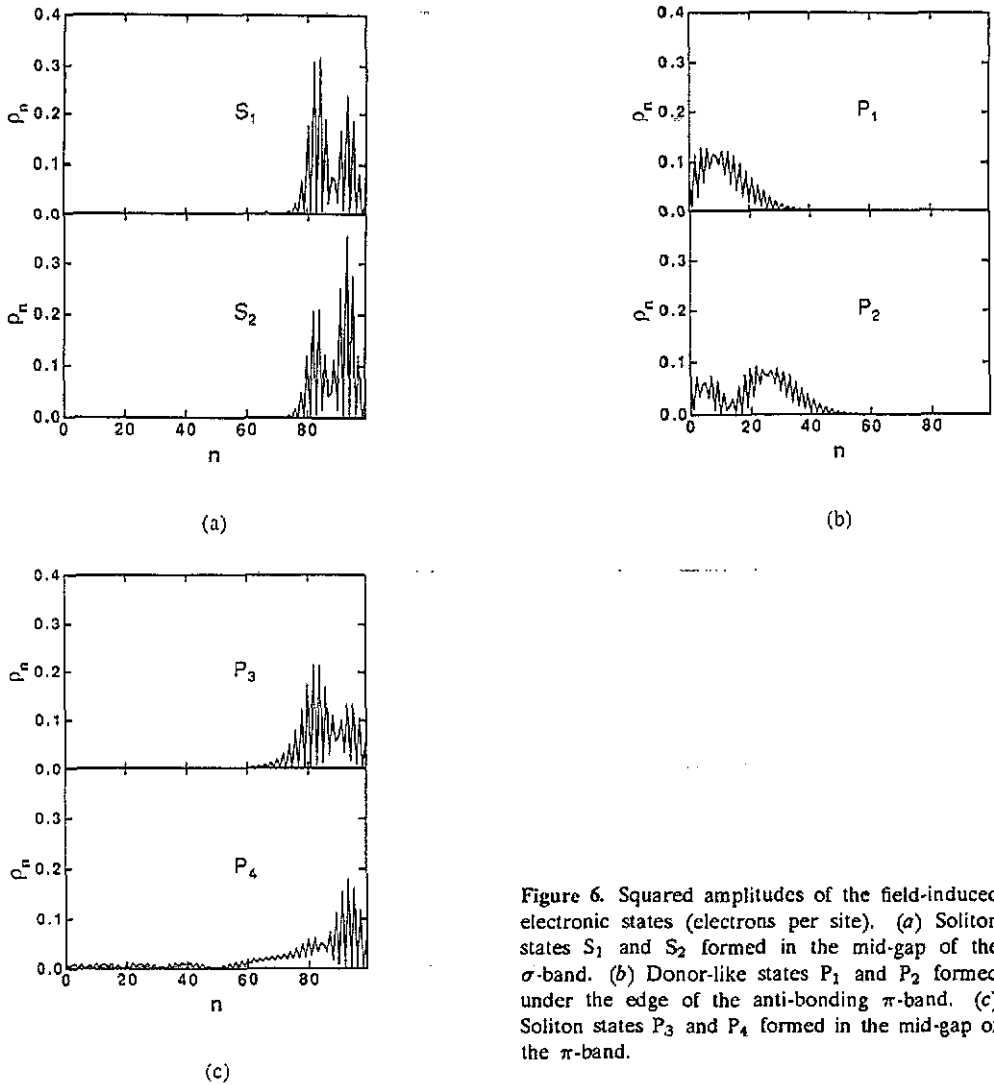
(a)

(b)

(c)

Figure 6. Squared amplitudes of the field-induced electronic states (electrons per site). (a) Soliton states S_1 and S_2 formed in the mid-gap of the σ-band. (b) Donor-like states P_1 and P_2 formed under the edge of the anti-bonding π-band. (c) Soliton states P_3 and P_4 formed in the mid-gap of the π-band.

these asymmetric responses of the step structure to the electric field in this work are obtained from the calculations for a striped structure, in which we do not take account of the alteration of the S_A and S_B steps. However, what we have considered here is the charge accumulation or depletion near S_A step edges. The use of the striped structure corresponds to the approximation that regards the S_B steps just as sources or sinks of electrons. For further detailed discussion more realistic models will be needed. We now have studies under way into the field-induced responses of a staircased structure.

4. Conclusion

We have investigated the structural stability of single-layered steps on Si(001) 2×1 surfaces under static electric fields. A stripe structure bounded by S_A-type steps
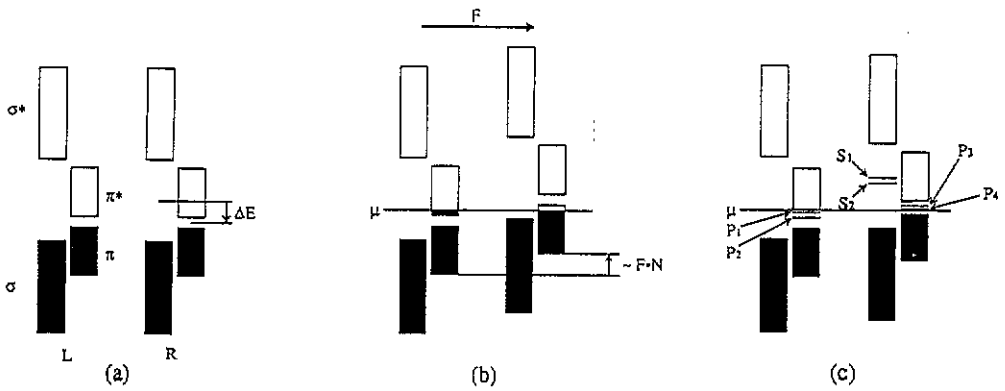
Figure 7. Schematic illustrations of π- and σ-bands near chain edges. (*a*) The perfectly dimerized state when $F = 0$. L and R stand for the left-hand and right-hand edges of the chain, respectively. Filled bands are represented by closed boxes while empty bands by open ones. (*b*) The perfectly dimerized state when $FN > E_g(\pi)$. We note that the direction of the electric field is from left to right in the figure. π-electrons are transferred from the right to the left edge of the chain without modification of the band structure. In this situation, substantial weakening of the dimer bands does not occur. (*c*) The asymmetric soliton structure. Both π- and σ-originated soliton levels P_3, P_4, S_1 and S_2 appear on the right edge of the chain. Donor-like states P_1 and P_2 appear on the left edge of the chain.

was considered and modelled by a one-dimensional chain which is stretched in the direction of a dimer bond. In order to describe the π- and σ-bands of the Si(001) 2×1 surface, we considered two bands with different band widths and energy gaps in the tight-binding method. The difference in the positions of the energetic centres of mass of the two bands was taken into account as the cause of the asymmetric behaviour of the system. Both the electronic and geometric degrees of freedom were optimized in the Born–Oppenheimer approximation to find out the ground-state solutions as a function of the external field. We found that the asymmetric distortion of the lattice occurs above a certain threshold field. The asymmetry is characterized by excitations of a soliton pair positioned on one step edge of the stripe. Substantial weakening of the dimer bonds is observed where the solitons are formed. From the analysis of the charge distribution and the local number of states, we found that the soliton pair is created by formation of the mid-gap states of both π- and σ-bands, which are filled with holes. Therefore the asymmetric structure is caused by the electron transfer from the π- and σ-bands on one edge to the anti-bonding π-band on the other edge of the stripe. Exact reversal of the asymmetry of the structure is realized by changing the sign of either ΔE or F. Our findings suggest the necessity of taking into account the field-induced changes in the electronic states near the step edges when interpreting experimental results of the current-induced conversion of the major domains on Si(001) 2×1 vicinal surfaces.

Acknowledgments

Appendix. ν-dependence of $N_\nu(n,m)$ when $F = 0$

The local number of states $N_\nu(n,m)$ which is defined as

$$N_\nu(n,m) = \sum_{l=n}^{m} |\langle l|\nu\rangle|^2 \tag{A1}$$

where $|\nu\rangle$ is the eigenstate and l is the site index, has the value of 1/2 if $n = 0$ and $m = N/2 - 1$ (N is an even number) when $F = 0$. In order to show this, we first note that the probability amplitude is distributed symmetrically,

$$|\langle n|\nu\rangle|^2 = |\langle N - n|\nu\rangle|^2. \tag{A2}$$

Therefore we have

$$\sum_{n=0}^{N/2-1} |\langle n|\nu\rangle|^2 = \sum_{n=N/2}^{N-1} |\langle n|\nu\rangle|^2 \quad \text{or} \quad N_\nu(0, N/2 - 1) = N_\nu(N/2, N - 1). \tag{A3}$$

From the normalization condition,

$$\sum_{n=0}^{N-1} |\langle n|\nu\rangle|^2 = 1 \tag{A4}$$

we immediately obtain the relation (see figure 4(*a*))

$$N_\nu(0, N/2 - 1) = N_\nu(N/2, N - 1) = \tfrac{1}{2}. \tag{A5}$$

Since the eigenvectors $|\nu\rangle$ form a complete set, we have

$$\sum_{\nu=1}^{N} |\langle n|\nu\rangle|^2 = \sum_{\nu=1}^{N} \langle n|\nu\rangle\langle\nu|n\rangle = 1. \tag{A6}$$

Therefore we obtain (see figure 4(*b*))

$$\frac{1}{N} \sum_{n=0}^{m-1} \sum_{\nu=1}^{N} |\langle n|\nu\rangle|^2 = \frac{m}{N}. \tag{A7}$$

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