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Local Electronic Structure of Si Semiconductor Surface *1

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Local electronic structure around Si-adatoms on Si(111)-7 × 7 surface has been investigated using the methods of STM (scanning tunneling microscopy), STS (scanning tunneling spectroscopy) and the molecular orbital calculation for the cluster of local structure around each adatom. In view of the difference of surrounding local structure, the adatoms are classified into four types, *i.e.*, the corner- and center-adatoms in a faulted half (F) cell, and the corner- and center-adatoms in an unfaulted half (UF) cell. In the STS spectra for each type of adatoms, significant differences are revealed. The intensity of the STS spectrum near the HOMO (highest occupied molecular orbital) level for a coner- and center-adatoms in the F cell is larger than for the respective adatoms in the UF cell. The calculation of local electronic structure indicates the main constitution of the HOMO by the atomic orbitals of adatoms and rest-atoms and also the charge transfer from the adatom to the rest-atom. The charge transfer leads to the intensity difference in the STS spectra near the HOMO between corner- and center-adatoms, because the corner- and center-adatoms have one and two rest-atom neighbors, respectively. The energy gap between the HOMO and LUMO (lowest unoccupied molecular orbital) in STS spectra for the corner-adatom in a F cell is larger than that in an UF cell. Similar results are obtained for the center-adatom. The change of the energy gap by the presence of stacking fault is demonstrated by the calculation using the cluster models with and without the stacking fault.

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1. Introduction

The surface analysis with atomic resolution has become possible by the development of scanning probe microscopes (SPM)[1–3] which usually provide the STS (scanning tunneling spectroscopy) for the measurement of the LDOS (local density of states) on the surface as well as the STM (scanning tunneling microscopy) for the observation of surface structure.

In recent years, various semiconductors have been employed as the parts of electronic devices. The parts are mostly formed through the adsorption and diffusion phenomena on the surface of substrates or deposited layers. To understand such phenomena, the bonding states of surface adatoms must be clarified in connection with their configurational and electronic structures. Numerous STM studies so far have been reported on semiconductors.[4–11] In particular, there have been many reports on the experimental and theoretical analysis of the reconstructed Si(111)-7 × 7 surface.[4–6,9–11] However, little attempt has been made to analyze the electronic states on the particular adatoms in connection with their net charge, energy gap and state density.

In the present study, the effect of atomic arrangement on the local electronic structure around each adatom is examined on the reconstructed Si(111)-7 × 7 surface by means of the STM and the atom-resolved STS. To clarify the cause of the configurational effect, molecular orbital (MO) calculation is carried out on the cluster of local structure around each adatom. The change of the electronic state density and energy gap by the difference of local structure around adatoms is discussed on the basis of experimental and calculated results.

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2. Experiment Procedure

The heat treatments and STM measurements were performed with an Omicron SPM system under the ultrahigh vacuum (UHV) of the pressure $< 1 \times 10^{-8}$ Pa. The STM tips were prepared from tungsten wire by electrochemical etching in a 2N-NaOH solution. The tips were annealed to degas before measurements. The Si samples used ($13.0 \times 3.0 \times 0.5\,mm^3$) were cut from phosphorus-doped (0.375–0.625 Ωcm) Si(111) wafers. The samples were flashed up to 1450 K to get clean surface by direct current heating. In order to make the 7 × 7 reconstruction of the Si(111) surface, the sample temperature were decreased to 1200 K and then slowly cooled down to room temperature. All heat treatments were made in the UHV chamber.

The STM measurements were performed at room temperature in the constant-current mode with tunneling currents between 1.0 and 2.0 nA, and sample voltages between −2.0 and 2.0 V. The STS measurements were done at each adatom on the 7 × 7 surface simultaneously with STM measurements. The LDOS and the energy gap were obtained from $(dI/dV)/(I/V)$–V curves which were automatically computed from measured I–V relations.

To examine the observed LDOS features, electronic structure on each adatom was also calculated using the discrete variational (DV) Xα molecular orbital method. We made at first the 7 × 7 unit cell model using the atomic coordinates reported by Qian and Chadi.[12] The clusters used in this calculation were cut out from the 7 × 7 unit cell. Except for the surface atoms (adatoms and rest-atoms), the ends of the cluster were terminated with hydrogen atoms to prevent surface effect. From the calculated results, we obtained various features of local electronic structure for particular atoms; *i.e.*, the state density, the energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), and the net charge.

3. Results and Discussion

Atomic images were observed on the reconstructed Si(111)-7 × 7 surface under the conditions of occupied and unoccupied states by STM. Figure 1 shows the adatom arrangement of STM images taken under the condition of occupied states. It can be seen that the brightness of adatoms is different each other. In view of the difference of surrounding local structure, the adatoms on the Si(111) surface can be classified into four types, *i.e.*, the corner- and center-adatoms in a faulted (F) half cell, and the corner- and center-adatoms in an unfaulted (UF) half cell. As is seen from Fig. 1, adatoms in the F half cell are brighter than those in the UF half cell. In a given half cell, corner-adatoms are brighter than center-adatoms. The result indicates that the tunneling current at an adatom site in the F half cell is larger than that in the UF half cell and, in a given half cell, the current at a corner-adatom site is larger than that at a center-adatom site. The difference in the tunneling current is closely related to that in the local electronic structure. Figure 2 shows the STS spectra taken at each adatom site. Significant differences are seen in the shape of the STS spectra for each type of adatoms. In the negative energy region, the spectra for the corner-adatom sites (1 and 4) apparently differ from those for the center-adatom sites (2 and 3). In each half cell, the intensity of the STS spectrum near the HOMO level for corner-adatoms (1 and 4) is higher than that for the center-adatoms (2 and 3). The STS intensity near the HOMO level for corner adatoms in the F half cell is slightly higher than that in the UF half cell. The difference in the STS intensities between the corner- and center-adatoms seems to result from the change of the occupied state density by charge transfer. Avouris and Wolkow[13] have suggested the possibility of the charge transfer from adatoms to rest-atoms as the cause of the different reactivity of each adatom with NH_3. Center-adatoms have two rest-atom neighbors, while corner-adatoms have only one. The different number of rest-atom neighbors may lead to the greater charge transfer to rest-atoms from center-adatoms compared with that from corner-adatoms, resulting in the lower STS intensity around the HOMO level for center-adatoms compared with that for corner-adatoms. To ascertain those aspects, we calculated the net charge for adatoms and rest-atoms using the MO method. In this calculation, two types of cluster models were used, *i.e.*, the corner model ($Si_{25}H_{34}$) locating a corner-adatom at the top center, and the center model ($Si_{26}H_{34}$) locating a center-adatom at the top center. In the corner model, the net charges for the corner adatom and the rest-atom are obtained as 0.07 and −0.09, respectively. In the center model, the net charges for the center-adatom and the rest-atom are 0.09 and −0.13, respectively. Therefore, it is evident that the charge transfer from adatoms to rest-atoms takes place and the electron release from the center-adatom (0.09) is more intense than that from the corner-adatom (0.07).

As described above, the shape and intensity of the STS spectra depend on the presence of stacking fault in a half cell. Energy gaps for each adatom in the half cells with and without stacking fault were estimated from the STS spectra. The results are shown in Table 1. The energy gaps at corner- and center-adatoms in the half cell with stacking fault (F half) are larger than those without stacking fault (UF half), respec-

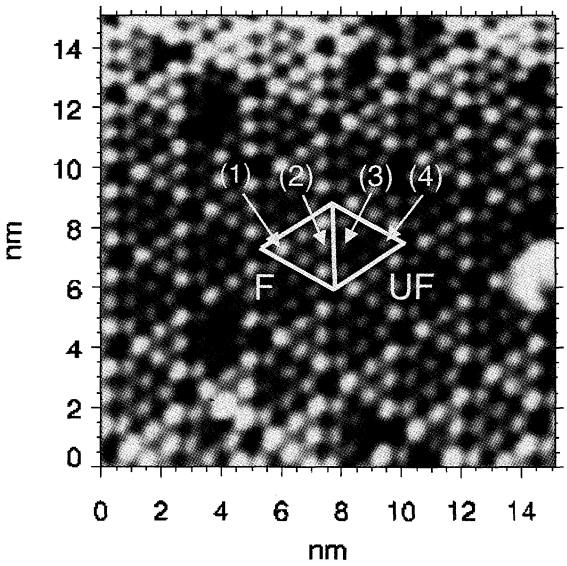

Fig. 1 STM image (15×15 nm^2) of the clean Si(111)-7×7 surface obtained under the condition of occupied states with tunneling current 0.15 nA and junction bias of −1.41 V at room temperature. The numbers of (1), (2), (3) and (4) correspond to the F half corner-adatom, the F half center-adatom, the UF half center-adatom and the UF half corner-adatom, respectively.

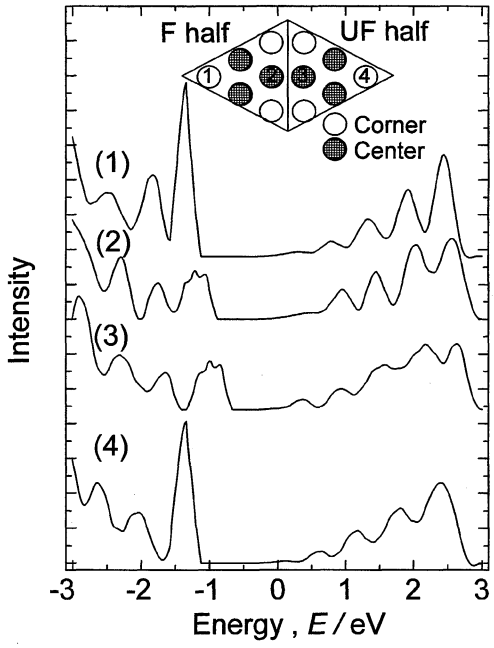

Fig. 2 STS spectra for adatoms on the clean Si(111)-7 × 7 surface and schematic illustration of adatom sites. Open circles are corner-adatoms and hatched circles are center-adatoms. (1): spectrum at the F half corner-adatom site, (2): spectrum at the F half center-adatom site, (3): spectrum at the UF half center-adatom site, (4): spectrum at the UF half corner-adatom site.

Table 1 Comparison of energy gap at adatom sites between experiment and calculation. (Unit:eV).

	STS result		Calculated result	
	F half	UF half	F half	UF half
Corner-adatom	1.24	1.01	1.33	1.23
Center-adatom	0.88	0.64	1.48	1.35

tively. Further, the energy gap at a corner-adatom is larger than that at a center-adatom in both half cells. The local electronic structure was calculated for four types of the clusters with adatoms using the MO method. The cluster models are shown in Fig. 3. Figure 4 shows the calculated electronic state density where each HOMO level is taken as 0 eV. The energy gaps obtained from the calculation are listed in Table 1. As can be seen from Table 1, the energy gap for the cluster with stacking fault (F half) is larger than that without stacking fault (UF half). This trend agrees qualitatively with that of STS measurement. However, the energy gaps calculated for the center adatom is too large compared with that obtained from the STS measurements. This disagreement may result from the smallness of center-adatom clusters, because the center adatom has two rest-atom neighbors. Nevertheless, it is not clear how large region beneath the surface has a substantial influence on the STS spectrum. Further the spectrum depends on various factors such as the STM tip shape and the tip-surface separation. Therefore, the LDOS of STS measurements does not directly correspond to the calculated state density (Fig. 4) at the adatom site of each cluster. The quantitative correspondence between measured and calculated LDOS is the future subject to be investigated.

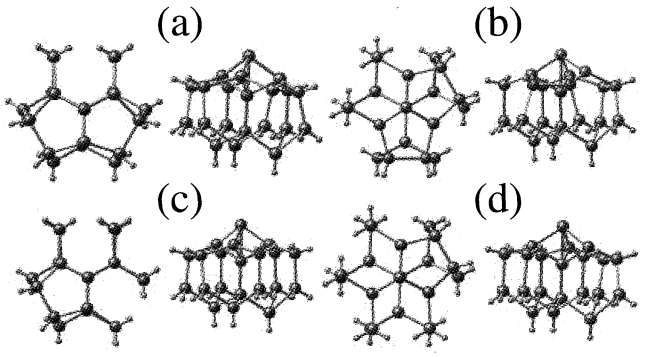

Fig. 3 Top and side views of cluster models used for MO calculation; (a) F half corner-adatom cluster ($Si_{21}H_{25}$), (b) UF half corner-adatom cluster ($Si_{21}H_{25}$), (c) F half center-adatom cluster ($Si_{21}H_{24}$), and (d) UF half center-adatom cluster ($Si_{21}H_{24}$).

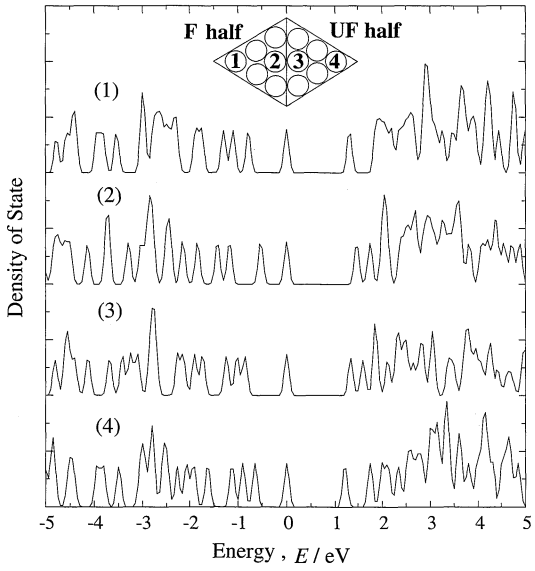

Fig. 4 Distributions of electronic state density for adatom clusters calculated by the molecular orbital method; (1) F half corner-adatom cluster, (2) F half center-adatom cluster, (3) UF half center-adatom cluster, and (4) UF half corner-adatom cluster.

The relative tunneling current can be roughly estimated from the integration of the calculated state density from Fermi level to -1.41 eV. The estimated relative currents were in the order as follows: F half corner-adatom>F half center-adatom>UF half corner-adatom>UF half center-adatom. This order agrees with that for brightness of the STM image shown in Fig. 1.

4. Conclusion

Interrelation between LDOS and local structure around adatoms on the reconstructed Si(111)-7 × 7 surface has been investigated using STM, STS and MO calculation method. The intensity of STS spectrum near the HOMO level for the corner-adatom is stronger than that for the center-adatom. The result of MO calculations indicates that the charge transfer to rest-atoms from center-adatoms is larger than that from corner-adatoms, thereby causing the weaker STS intensity around the HOMO level for the center-adatoms compared with that for the corner-adatoms. In the STS spectra, the energy gap between HOMO and LUMO for a corner- or center-adatom in the F half cell is larger than that in the UF half cell. Such difference was also demonstrated by the molecular orbital calculation using four types of the adatom cluster models.

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