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SELF-CONSISTENT DV-Xα CLUSTER CALCULATION OF ELECTRONIC STRUCTURE OF THE Si (111)-7×7 MODEL SURFACE

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Theoretical information is provided on the electronic structure for various reconstruction models for the Si(111)-7×7 surface. The first principle DV-Xα calculations are carried out for the surface cluster without a vacancy $Si_{16}H_{21}$ and for that with a vacancy $Si_{15}H_{21}$. The low-density vacancy model recently proposed by Ino is pointed out to be a promising reconstruction model for the Si(111)-7×7 surface.

The long-period reconstruction found in the Si(111)-7×7 surface has received much theoretical as well as experimental interest. The earliest reconstruction model was proposed by Lander [1]. The Lander model includes 13 vacancies (26.5 % vacancy sites) in the unit cell accompanied by the resultant formation of warped benzene rings. The recent intensity analysis by Ino on RHEED patterns [2] indicated the presence of only 3 vacancies (6.1 % vacancy sites) placed to form a regular triangle in the unit cell. Kinematical studies also made by Ino [2] on the LEED-IV spectra for the (0,0) beam supported the above indication, though further careful investigations such as those of dynamical effects are necessary.

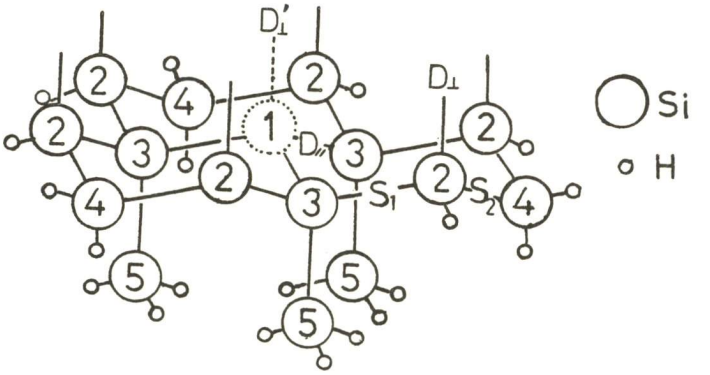

Fig.1 Surface clusters $Si_{16}H_{21}$ including Si(1) and $Si_{15}H_{21}$ without it. $D_\perp$ ($D'_\perp$) and $D_{//}$ denote P_z-like and P_x, P_y-like dangling bonds, respectively. S_1 and S_2 denote back bonds.

On the other hand, Chadi et al proposed in their recent letter [3] a buckled ring-like structure for the 7×7 surface, emphasizing the 2×1-like electronic structure [4] of the 7×7 surface. It is pointed out [5], however, that the Chadi et al's model cannot reconcile with the Patterson function derived from intensity analyses of RHEED. Thus,

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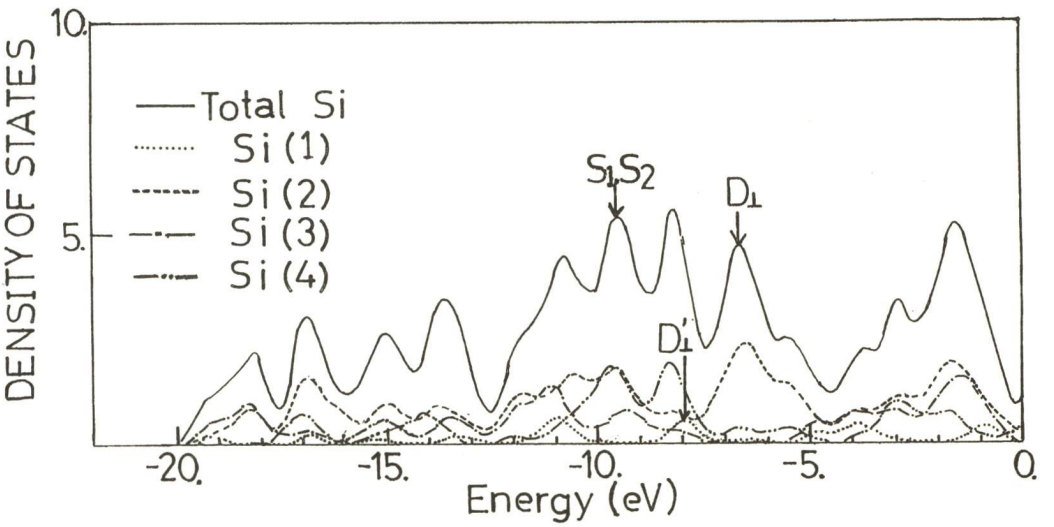

Fig.2 Spectrum for the buckled system (A) $Si_{16}H_{21}$ with six Si(2) atoms lowered by 0.5 a.u. from the bulk equilibrium positions

at present no decisive atomic arrangement on the 7×7 surface has yet been established.

In this paper we shall present theoretical information on the electronic structure for various reconstruction model of the Si(111)-7×7 surface. We carry out the first principle DV-Xα cluster calculations, in contrast to the previous tight binding calculations by Pandey[6]. We concentrate ourselves to the surface cluster without a vacancy (A) $Si_{16}H_{21}$ and that with it (B) $Si_{15}H_{21}$ (see Fig.(1)). Both of them have C_{3v} symmetry. Studies are made both for nonrelaxed and relaxed cases of these systems. But, in what follows, we shall confine ourselves to the buckled system A and for the system B with Si (3) atoms in Fig.(1) nearest to the vacancy displaced towards it.

Calculated spectra of both total and local state densities for systems A and B are given in Figs.(2) and (3), respectively. Firstly we have found in our calculations following characteristics common to both the systems A and B; (i) A dangling bond surface state $D_\perp$ lies slightly above the valence band top. (ii) The peak position of $D_\perp$ is sensitive to the relaxation of the top-most layer: in both the systems, lowering six Si(2) atoms in Fig.(1) by 0.5 a.u. (33 % of the interlayer spacing) from the bulk equilibrium positions, we have found the peak position of $D_\perp$ to be shifted 1.5 eV upwards. Other structures in the spectra, however, do not show any essential change.

Secondly we find in Fig.(2); (i) For the buckled system A, there exists a peak $D'_\perp$ of the local state density of Si(1) atom about 1.5 eV below the main peak $D_\perp$ associated with Si(2) atoms. This peak $D'_\perp$ represents a S-like dangling bond surface state of the Si(1) atom. (ii) The peaks S_1, S_2 about 1.5 eV below $D'_\perp$ are attributed to back-bond states indicated in Fig.(1) in the presence of buckling. We

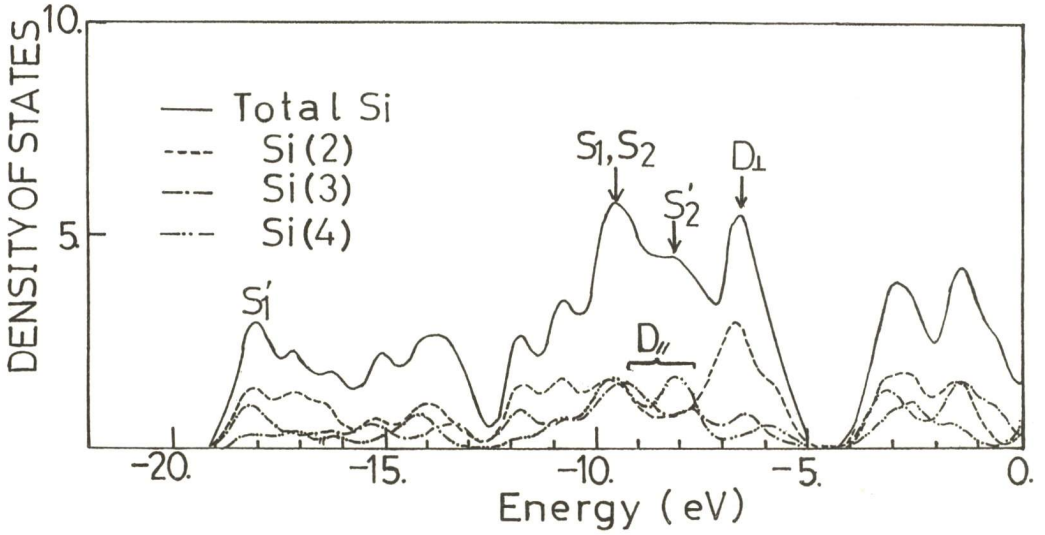

Fig.3 Spectrum for the system (B) $Si_{15}H_{21}$ with the same relaxation as in the system A

also have calculated the spectrum for the system with Si(1) atom raised, finding that features (i) and (ii) are not essentially changed. It should be noted that the calculated spectrum for the system A does not well agree with recent UPS results [3], [7], [8].

Thirdly we find in Fig.(3); (i) For the system B, there appears a doubly-humped structure $D_{//}$ associated with the local state density of Si(3) atoms located at 2.5 eV below the peak $D_{\perp}$. This structure is mainly consisted of Px, Py-like orbitals of Si(3) atoms directed towards the vacancy. The energy range of $D_{//}$, however, closely overlaps with those of enhanced back-bond states S_1 and S_2 as defined in Fig.(1). (ii) Another peak S_1' is also found near the valence band bottom. It is associated with the back-bond state S_1 modified by the presence of a vacancy. The observed enhancement of this peak indicates the presence of a trend to form a double bond as pointed out by Lander [1]. (iii) The peak S_2' 1.5 eV below $D_{\perp}$ is due to the back bond S_2 modified by the presence of a vacancy.

The energy positions of $D_{\perp}$, S_2' and $D_{//}$ in the system B are in good agreement with recent UPS experiments [3], [7], [8]. Therefore, we proceed to compute the spectrum for the system B' where the top-most layer is lowered to the same level as that of the second one with the length of the bond nearest to the vacancy being fixed to be 4.44 a.u.. The spectrum thus calculated is given in Fig.(4), showing that the $D_{//}$ structure is sharpened around the energy position 2.5 eV below the peak $D_{\perp}$. The spectrum for the system B' agrees better with recent UPS results [3], [7], [8]* The angle-resolved UPS [7], [8], however, does not confirm the presence of Px, Py-like dangling bond states. This fact may be explained as follows; The number of this kind of bonds in the system B' amount to 33 % (3/9) of the

* A possibility cannot be denied that the calculation for the system A reproduces the UPS results, if one assumes different degree of buckling.

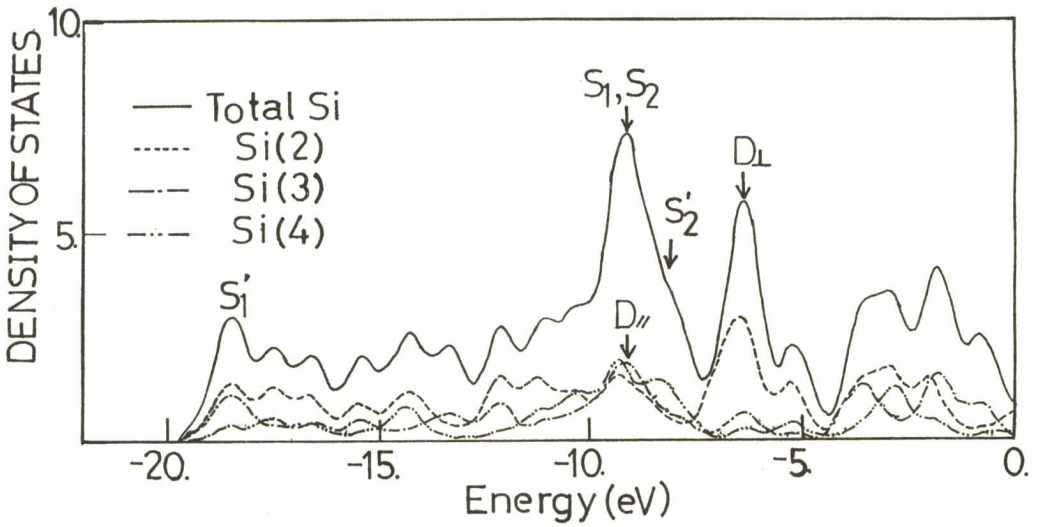

Fig.4 Spectrum for the system (B') $Si_{15}H_{21}$ with the top-most layer being lowered to the same level as the second one

total number of dangling bonds on the surface, while this ratio is merely 16 % (9/55) in the low-density vacancy model recently proposed by Ino [2]. This shows that our calculated intensity of $D_{//}$ should be decreased in comparing with the experiments.

In conclusion, we have found that the low-density vacancy model is a promising reconstruction model of the Si(111)-7×7 surface reproducing well the recent UPS spectrum.

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