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Structural study of the Si–alkali-metal interface with x-ray standing waves

S. Lagomarsino, F. Scarinci, P. Castrucci,* and C. Giannini†
Istituto di Elettronica dello Stato Solido, CNR, V. Cineto Romano, 42 00156 Roma, Italy

E. Fontes and J. R. Patel
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

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X-ray standing-wave measurements on Cs and Rb adlayers on the Si(111)7×7 surface are presented. Low [≈0.06 monolayer (ML)] and medium (≈0.15 ML) coverages have been analyzed. The (111) and the $(\bar{1}11)$ reflections have been used. Since the experimental results clearly indicate that multisite occupancy takes place, the threefold hollow (H_3), the threefold filled (T_4), and all the dangling-bond sites have been considered as possible adsorption sites. Distinction has been made between the faulted and the unfaulted half of the 7×7 cell. The Si–alkali-metal bond length has been assumed to be the sum of the covalent radii of the two elements. Our results indicate that both Rb and Cs adsorb preferentially on the H_3 and the T_4 sites. The remaining atoms adsorb most at the atop sites for Rb and at the adatom sites (i.e., on top of the silicon adatom) for Cs.

The alkali-metal–Si interface has received much interest in the last five years from both a fundamental and an applied point of view because of the special character of the interaction between the alkali-metal atoms and the silicon ones. This gives rise to interesting phenomena such as the large enhancement in the oxidation rate of the Si substrate when covered with alkali metals[1–4] and the ability of thin intralayers of alkali-metal atoms to control the band offsets in heterojunctions and in insulator-semiconductor interfaces.[5]

Despite this interest, the adsorption site of the alkali metals on the Si surface is an open question. Most experimental and theoretical work on this point has been on the (100)2×1 Si surface,[6–8] but even in this case there is no agreement between different adsorption models. Concerning the (111)7×7 Si surface, experimental work has been carried out with reflection high-energy electron diffraction (RHEED) for Li and K (Ref. 9) and with scanning tunneling microscopy (STM) for Li,[10] K, and Cs.[11,12] From the RHEED study on K it has been proposed that K is absorbed on top of the 19 dangling bonds of the 7×7 reconstruction[9] following the dimer-adatom-stacking (DAS) fault reconstruction model.[13] STM measurements indicated a preferential adsorption at one of the center adatom sites at very low coverage [less than about 0.01 monolayer (ML)][12] mainly on the faulted half of the 7×7 cell and the formation of trimers at coverages less than 0.1 ML.[10,12] At higher coverages (more than about 0.1 ML) the unfaulted half becomes occupied and clusters composed of six or nine atoms were formed.[10] Recently also x-ray standing-wave measurements have been carried out on this kind of interface.[14,15] Discussions of the[14,15] authors' results will follow.

For each set of planes considered, the x-ray standing waves give the location P of the adsorbed atoms with respect to the bulk lattice plane under consideration, and the fraction F of the atoms that occupy that position.[16] With two lattice planes, triangulation is, therefore, possible and the position of the adsorbed atoms with respect to the substrate atoms can be determined.[17] If more than one site is occupied, a resulting position P and a resulting fraction F are obtained, related to the position P_i and the probability f_i of the individual sites in the following way:[18]

$$\tan(2\pi P)=\frac{\sum_i f_i \sin(2\pi P_i)}{\sum_i f_i \cos(2\pi P_i)}\ , \tag{1}$$

$$F=f_{\rm com}\left\{\left[\sum_i f_i \sin(2\pi P_i)\right]^2+\left[\sum_i f_i \cos(2\pi P_i)\right]^2\right\}^{1/2}\ , \tag{2}$$

with $\sum_i f_i=1$ and where $f_{\rm com}$, whose value can range between 0 and 1, is a factor related to the static and dynamic (thermal vibration) disorder. The higher the disorder, the smaller the value of $f_{\rm com}$.

The values of P and F are experimentally determined by measuring the fluorescence intensity $Y(\theta)$ from the adsorbate as a function of the Bragg angle θ during Bragg diffraction. $Y(\theta)$ is given by

$$Y(\theta)\propto 1+R(\theta)+2\sqrt{R(\theta)}F\cos[\nu(\theta)-2\pi P]\ . \tag{3}$$

$R(\theta)$ is the Bragg reflectivity, $\nu(\theta)$ is the phase between the incident and the diffracted wave fields. The $Y(\theta)$ value is normalized to 1 far from the angular diffracting region. F and P are the free parameters in the fitting of the experimental curve with the calculated dependence of Y on θ expressed by Eq. (3).

We performed the experiment at the AT&T beam line X15A at the National Synchrotron Light Source in Brookhaven. Both preparation of the sample and the x-ray standing-wave (XSW) experiment were performed in ultrahigh vacuum (10^{-10} Torr).[19] The 7×7 surface reconstruction was obtained by heating to about 850 °C a crystal previously cleaned with the Shiraki treatment.

TABLE I. Experimental results (P_{111}, F_{111}, $P_{\bar{1}11}$, and $F_{\bar{1}11}$) for different alkali metals and coverages Γ.

	Γ (ML)	P_{111}	F_{111}	$P_{\bar{1}11}$	$F_{\bar{1}11}$
Rb	0.05	1.03±0.02	0.33±0.05	0.74±0.04	0.22±0.05
Rb	0.16	1.08±0.02	0.49±0.05	0.71±0.04	0.16±0.05
Cs	0.07	0.94±0.02	0.53±0.05	0.76±0.04	0.28±0.05
Cs	0.14	0.95±0.02	0.36±0.05	0.70±0.04	0.31±0.05

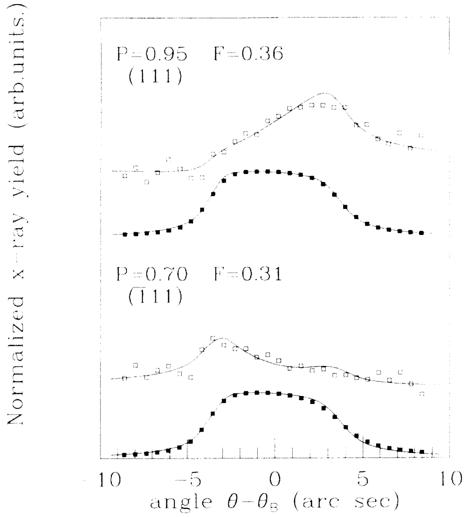

FIG. 1. X-ray standing-wave Cs results for (111) and ($\bar{1}$11) diffracting planes. Open square: fluorescence yield. Filled square: diffracted intensity. Solid lines are theoretical fits to the experimental data.

Sharp low-energy electron diffraction (LEED) patterns and Auger spectra free of contaminants were obtained after reconstruction. The alkali metals were evaporated onto the sample held at room temperature from carefully outgassed dispensers produced by SAES getters. Low (≈0.07 ML) and medium (≈0.15 ML) coverages, (1 ML$=7.83\times10^{14}$ atoms/cm^2) of Cs and Rb were studied. The coverage was measured using both the relative intensities of the Auger lines (Rb and Cs with respect to Si) and the relative intensities of the x-ray fluorescence peaks (Rb $K\alpha$ or Cs $L\alpha$ with respect to Si $K\alpha$). The absolute coverage was obtained by comparing the fluorescence intensities with those obtained on a sample capped with Si and analyzed with Rutherford backscattering. We used both (111) and ($\bar{1}$11) diffracting planes. The former set of planes is parallel to the surface, while the latter set of planes forms an angle of 70.54° with the surface. For these planes the scattering geometry is of the same kind as described in Ref. 17. Table I summarizes the experimental results. Figure 1 shows the typical spectra for both (111) and ($\bar{1}$11). From an analysis of Table I some observations can be made.

(i) The coherent fraction is never larger than about 0.5. This is a well-reproducible result and clearly indicates that more than one site is occupied.

(ii) The results are quite similar for both Rb and Cs and for all the coverages. This indicates a common behavior for the two elements and the existence of multisite occupancy even at low coverage.

As already reported in our previous paper the LEED pattern after deposition of the alkali metal still retains the 7×7 symmetry with only some changes in the relative intensity of some spots. No new reconstruction is, therefore, induced by the alkali metals, as observed also in the (100)2×1 case.[6] The starting point in the interpretation of the XSW experimental data is therefore the DAS model of Takayanagi *et al.*[13] which foresees 19 dangling bonds (at adatom, atop, and vacancy sites). Intuitively one can expect that the alkali metals, being monovalent, are adsorbed on top of the dangling bonds. However, as established in Ref. 14, the XSW measurements from the (111) diffracting planes are not compatible with such a model because in this case the alkali-metal–Si bond length would be too short (1.8 Å) or too long (5 Å). Surface-extended x-ray absorption fine structure measurements on K on Si(100) showed a value of the K-Si bond length of 3.14 Å, equal to the sum of the covalent radii.[21] Also the ($\bar{1}$11) results reported in Table I exclude the possibility of adsorption only on top of the 19 dangling bonds. In addition to them, we have, therefore, considered the threefold hollow site (H_3) and the threefold filled site (T_4). To allow adsorption on the threefold sites the adatoms must desorb in order to leave enough space and available Si bonds to the alkali metals. Figure 2 shows the sites under consideration. In the DAS model, the stacking fault plays an important role. For the XSW there is no difference if the faulted and unfaulted sites are excited with the (111) reflection, but if excited with the ($\bar{1}$11) there is a marked difference in the case of the H_3 and the atop sites. The positions of Rb and Cs calculated for each different site are reported in Table II.

From the XSW measurements four parameters are determined: the positions P_{111} and $P_{\bar{1}11}$ and the coherent fractions F_{111} and $F_{\bar{1}11}$. These experimentally determined quantities must be compared, within the errors,

TABLE II. Expected Rb and Cs positions (in units of interplanar spacing) calculated according to Qian and Chadi (Ref. 20) coordinates for atop, adatom, and vacancy sites, and according to the bulk coordinates for H_3 and T_4 sites.

		H_3 fault	H_3 unfault	T_4	Atop fault	Atop unfault	Adatom	Vacancy
Rb	P_{111}	0.958	0.958	0.959	0.302	0.302	0.610	0.220
	$P_{\bar{1}11}$	0.171	0.849	0.510	0.951	0.297	0.726	0.263
Cs	P_{111}	0.999	0.999	0.999	0.340	0.340	0.648	0.258
	$P_{\bar{1}11}$	0.184	0.863	0.523	0.964	0.310	0.739	0.276

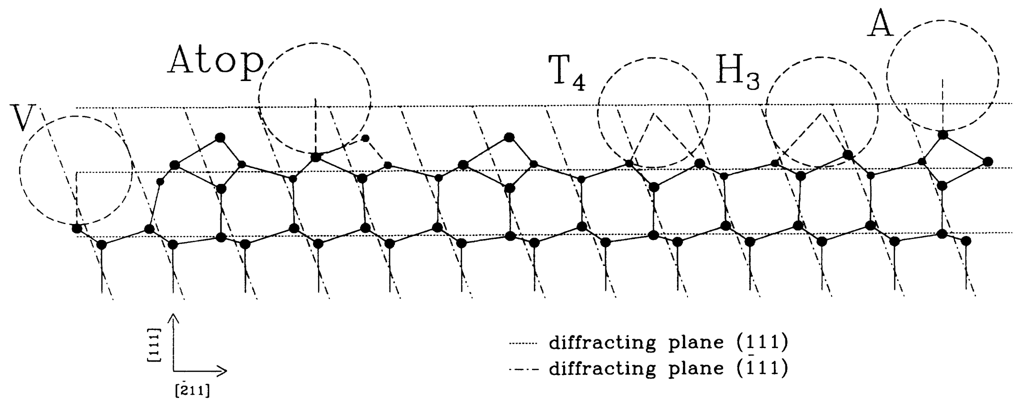

FIG. 2. ($\bar{1}$11) side view of the 7×7 cell reconstructed according to the DAS model and to Qian and Chadi (Ref. 20) calculations for the atom positions of the first four layers. The H_3, T_4, atop, adatoms (A), and vacancy (V) sites are indicated.

with the corresponding ones as they result from combinations of the sites under consideration: H_3 faulted, H_3 unfaulted, atop site faulted, atop site unfaulted, T_4, adatom site, and vacancy site (for the last three sites the standing waves cannot distinguish between the faulted and the unfaulted halves). We took into account the possible occurrence of a static and/or dynamic disorder, allowing the f_{com} value to vary between 1 and 0.6. If the bond length is taken as the sum of the covalent radii it turns out to be 3.52 Å for Cs and 3.40 Å for Rb. In Table III are reported the occupancies that give an agreement between the experimental values and the calculated ones for Rb and Cs coverages, respectively. Calculations have also been made considering other types of sites typical of the 7×7 reconstruction (the so-called large hollows and bridges) but for them very small occupation probabilities have been found.

From Table III the following appear.

(i) Different coverages relative to the same alkali metal have a similar site distribution.

(ii) The H_3 on the unfaulted half of the cell and the T_4 sites are occupied by both the alkali-metal atoms considered.

(iii) Some of the Rb atoms are at atop sites, mainly on the faulted half of the cell. In the low-coverage case there is also a small probability of adsorption at the adatom sites.

(iv) Some Cs atoms adsorb also on the adatom sites and, in the low-coverage case, on the faulted H_3 sites.

(v) In any case, the vacancy site has a small or zero occupation probability.

A difference in the behavior of the two halves of the cell has already been reported by Hasegawa and coworkers,[10–12] as discussed above.

The origin of the different distributions of Cs and Rb is not clear. Possible explanations may be related to the different atomic size or to the different evaporation conditions (5- and 7-A current for Cs and Rb dispenser, respectively).

Our conclusions are somewhat different from those presented by the authors in Ref. 15. They studied Cs high-coverage (0.6 ML) samples as-grown and after partial Cs desorption by thermal treatment, using the (111) and the (220) reflections. They obtained the result that a simultaneous occupation of T_4, H_3, and the atop sites (the last two mainly on the unfaulted half of the cell) takes place for the room-temperature sample, with an occupancy of 22% on the atop and of 42% on the threefold sites, without a quantitative distinction between T_4 and H_3. Conversely, they found that the unfaulted H_3 site is preferred after the annealing. It may be that the differences between our conclusions and theirs are due to somewhat different physical conditions. In fact, their measurements on as-grown samples refer to high cover-

TABLE III. H_3, T_4, and all the dangling-bond-site distributions that give an agreement between experimental and calculated results. The variability range of each site value is 0.05 and 0.10 for the ones with daggers. The errors on theoretical P and F equal the experimental ones.

	H_3 fault	H_3 unfault	T_4	Atop fault	Atop unfault	Adatom	Vacancy	$f_{\text{com}}\pm10\%$ (111)	($\bar{1}$11)	(111)	($\bar{1}$11)
Rb	0.00	0.30	0.30	0.20	$0.05^{\dagger}$	0.10	$0.05^{\dagger}$	0.75	0.69	$P=1.02$	$P=0.77$
0.05 ML										$F=0.44$	$F=0.33$
Rb	0.00	0.15	0.45	0.35	$0.00^{\dagger}$	0.00	$0.05^{\dagger}$	0.93	0.76	$P=1.07$	$P=0.72$
0.16 ML										$F=0.53$	$F=0.21$
Cs	0.20	0.30	0.20	0.00	0.00	0.30	0.00	0.95	0.74	$P=0.94$	$P=0.77$
0.07 ML										$F=0.56$	$F=0.38$
Cs	0.00	0.30	0.30	0.00	0.00	0.30	0.10	0.84	0.63	$P=0.96$	$P=0.71$
0.14 ML										$F=0.43$	$F=0.49$

age (0.6 ML), while the samples comparable in coverage with ours have been subjected to thermal treatment and, therefore, they are, in principle, different from the room-temperature depositions.

In conclusion, x-ray standing-wave measurement on Cs and Rb low and medium coverage on Si(111) 7×7 surface have been carried out. The measurements show occupancy of more than one site. The threefold hollow (H_3), the threefold filled (T_4), and all the dangling-bond sites have been considered as possible adsorption sites. The results point to a distribution where at least fifty percent of the alkali-metal atoms adsorb at the H_3 site on the unfaulted half of the cell and at the T_4 site, a large percentage of the other Rb atoms occupy the atop sites, mainly on the faulted half, and most of the remaining Cs atoms distribute at the adatom sites.

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[*] Present address: Universitá di Camerino, Dipartimento di Matematica e Fisica, via Madonna delle Carceri, 62032 Camerino (Mc), Italy.

[†] Permanent address: Centro Nazionale Ricerca e Sviluppo Materiali (CNRSM), 72023 Mesagne (Br), Italy.

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