X-ray standing-wave study of Cs/Si(111) 7×7

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The adsorption site of Cs on Si(111)7×7 has been investigated by using x-ray standing-wave fields. The (111) and (220) Fourier components of the Cs distribution function were measured for different Cs coverages and annealing temperatures. At saturation coverage (obtained for a layer deposited at room temperature) on-top and threefold sites are occupied by Cs atoms. Annealing cycles to 500 °C improve the ordering of the adlayer, and Cs atoms are adsorbed only at threefold sites. Annealing to higher temperatures (600 °C) is accompanied by a significant coverage reduction. A concomitant change in the observed position is observed which can be attributed either to occupation of a new site or to a coverage-dependent bond-length change.

I. INTRODUCTION

Alkali metals adsorbed on silicon surfaces have received widespread attention recently.[1] This is due to the fact that these interfaces constitute interesting model systems to study such important topics as Schottky-barrier formation, or metallization of deposited layers. To this end, the knowledge of the alkali-metal adsorption site is of great interest. Nevertheless, this important item has been the object of less effort than other properties of the interface. For Si(100)2×1 the adsorption site of alkali metals has been experimentally determined,[2,3] but the proposed site is still polemic. In the case of the well-known Si(111)7×7 surface, the adsorption of alkali metals has been studied by different techniques,[4-9] but no conclusive information about the adsorption site is available. In particular, for K/Si(111)7×7 a fairly disordered adsorption was observed.[8] The only exception is the Li/Si(111) (Ref. 10) case, but this particular alkali metal behaves in many respects in a different way from the other alkali metals.[11]

We have employed x-ray standing-wave fields (XSW) to determine the adsorption site of Cs on Si(111)7×7 for different conditions of coverage and annealing temperature. The XSW technique allows one to measure very precisely the distance between the adsorbed atoms and a certain bulk lattice plane.[12] A detailed explanation of the physical processes and theory involved in XSW experiments can be found in Ref. 13.

II. EXPERIMENT

The experiments were made at the station ROEMO I of the Hamburg Synchrotron Radiation Laboratory (HASYLAB), using synchrotron light from the storage ring DORIS. The white synchrotron light was monochromatized by a double-crystal setup. The experimental system consists of three permanently mounted ultrahigh-vacuum (UHV) chambers (base pressure 5×10^{-11} mbar) and has been described in detail elsewhere.[14]

The Si(111) samples were cut from p-type single crystals, and chemically treated before insertion in the chamber.[15] Once in UHV, the samples were annealed to 900 °C in a vacuum better than 5×10^{-10} mbar, after

long-time outgassing at 600 °C, and were cooled down at a rate less than 1 °C/sec. The Si(111) surfaces exhibited a sharp 7×7 low-energy electron-diffraction (LEED) pattern, without traces of contaminants as judged by Auger electron spectroscopy (AES). A clean Si(111)7×7 surface was exposed to Cs evaporated from a commercial source (SAES-Getters, Italy) up to surface saturation. The surface was then annealed to a certain temperature, checked by LEED/AES, and transferred into the analysis chamber to perform an XSW experiment. After 2–5 h the measurement was ready, and the sample was checked again by LEED/AES without observing significant changes. The coverage (Θ) was determined by comparing the L_α fluorescence signal of Cs with the K_α signal of Si. All coverages were measured with a 10% accuracy and are given in monolayers [ML, 1 ML $=7.83 \times 10^{14}$ atoms/cm^2, the atomic density of the bulklike Si(111) surface].

III. DATA ANALYSIS

In XSW experiments the sample reflectivity and the fluorescence emission from an adsorbate are simultaneously measured for a certain Bragg reflection, as a function of incidence angle. According to the dynamical theory of x-ray diffraction, the normalized fluorescence yield curve $Y(\theta)$ of an adsorbate will vary with the reflection angle θ as

$$Y(\theta) = 1 + R(\theta) + 2\sqrt{R(\theta)} f_c \cos[v(\theta) - 2\pi\Phi] ,$$

where $R(\theta)$ is the sample reflectivity for the (hkl) Bragg reflection, and $v(\theta)$ is the phase difference between the incident and the reflected wave.[16] The parameters f_c and Φ are obtained from the experimental fluorescence yield by fitting the upper expression to the experimental data. They determine the (hkl) Fourier component of the atomic density function of the fluorescence radiating adsorbate atoms, $F_{(hkl)} = f_{c,(hkl)} \exp(-2\pi i \Phi_{(hkl)})$. The phase Φ gives in a one-position model the distance of the adsorbed atoms to the diffracting plane (hkl) in units of lattice spacing (coherent position). The coherent fraction f_c is the relative number of atoms at the coherent position given by Φ.

IV. RESULTS AND DISCUSSION

The Si(111) surface was investigated by using the (111) reflection (diffracting planes parallel to the surface) and the (220) reflection (diffracting planes 35.26° to the surface). After Cs adsorption, the 7×7 reconstruction of the clean surface weakened, and only the first-order spots remained. After annealing to 500 °C, a 7×7 pattern reappeared, but only the first-order spots and the seventh-order spots closer to the first-order ones could be seen. After annealing to higher temperatures (up to 600 °C) no change was observed. The results for the (220) and (111) reflections appear in Table I together with the preparation conditions. The corresponding experimental curves are shown in Figs. 1, 2, and 3.

In order to determine the adsorption site, both information on the bond length and on the atomic structure of the reconstruction are necessary. We have taken experimental bond lengths from previous measurements on similar systems [K/Si(100), (Ref. 17)] and values provided by semiempirical models.[18] Considering that the K/Si experimental bond length fairly accurately reproduces the sum of covalent radii,[18] we assumed a Cs-Si bond length of 3.52 ± 0.1 Å for our analysis. The error bar accounts for possible errors in the bond-length determination, and also for possible bond-length changes due to the actual bonding geometry.[17,18] The atomic structure of the Si(111)7×7 reconstruction is fairly well known, although it is not clear how it could be affected by Cs adsorption. Figure 4 displays a schematic view of the reconstruction according to the model by Takanayagi et al.[19] Plausible adsorption sites on this surface are indicated in Fig. 4 as well. A corresponds to the on-top site. B and B_e are threefold (3F) sites. B is the normal one, and B_e a 3F site where Cs atoms eclipse the second silicon layer (sometimes called also T_4). Occupation of these sites should involve removal of adatoms to leave free the dangling bonds of the silicon atoms. Finally, C is an adatom on-top site: Cs atoms are adsorbed on top of the silicon adatoms of the 7×7 reconstruction. Note that sites A and B have different distances to the [220] lattice plane, depending on whether they correspond to the faulted or to the unfaulted half of the 7×7 unit cell. The expected distances for the

FIG. 1. Cs/Si(111)7×7, (220) reflection at 10.0-keV energy. Experimental data points and theoretical curves (all normalized) for the Cs L_a fluorescence yield (□) and silicon (220) reflectivity (+) as a function of reflection angle. From bottom to top are reflectivity, Cs fluorescence as deposited, and after 90 s at 450 °C (vertical offset =1). For details see Table I.

different sites appear in Table II (in the case of $d_{[220]}$, the values for the faulted and unfaulted halves appear also, together with the mean value that would be obtained for 50% occupation of faulted and unfaulted sites). These values have been normalized to the interval 0.5–1.5.

In view of the values of Tables I and II, we note that none of the possible sites agrees with the experimental results at saturation coverage (room temperature data). The coherent phase $\Phi_{(111)}$ lies between the values expected for the hollow (B, B_e) and on-top (A) sites, which could be indicative of simultaneous occupation of both

TABLE I. Experimental results for Cs/Si(111)7×7.

Treatment	Φ [a]	f_c [b]	Θ [c]	Θ_c [d]
	(111) reflection			
RT	1.08 ± 0.01	0.48 ± 0.03	0.61	0.29
90 s 450 °C	1.02 ± 0.01	0.47 ± 0.03	0.14	0.07
+300 s 500 °C	1.02 ± 0.02	0.50 ± 0.03	0.14	0.07
+1 s 600 °C	1.10 ± 0.02	0.44 ± 0.03	0.12	0.05
+2 s 600 °C	1.12 ± 0.02	0.71 ± 0.03	0.07	0.05
	(220) reflection			
RT	0.97 ± 0.04	0.17 ± 0.03	0.48	0.08
90 s 450 °C	0.81 ± 0.02	0.23 ± 0.03	0.28	0.08

[a] Φ, phase.
[b] f_c, coherent fraction.
[c] Θ, coverage (ML ± 10%).
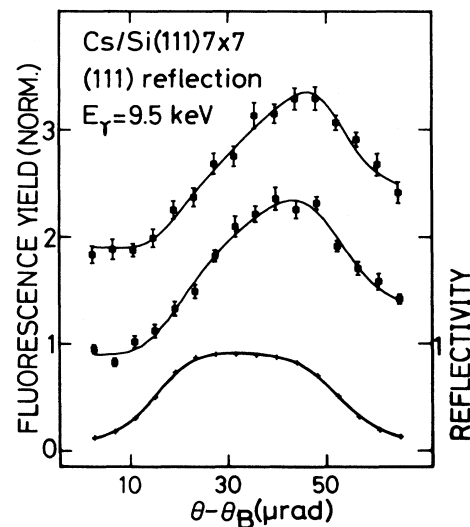[d] Θ_c, coherent coverage (ML ± 10%).

FIG. 2. Cs/Si(111)7×7, (111) reflection at 9.5-keV energy. Experimental data points and theoretical curves (all normalized) for the Cs L_a fluorescence yield (□) and silicon (111) reflectivity (+) as a function of reflection angle. From bottom to top are reflectivity, Cs fluorescence as deposited, and after 90 s at 450 °C (vertical offset =1). For details see Table I.
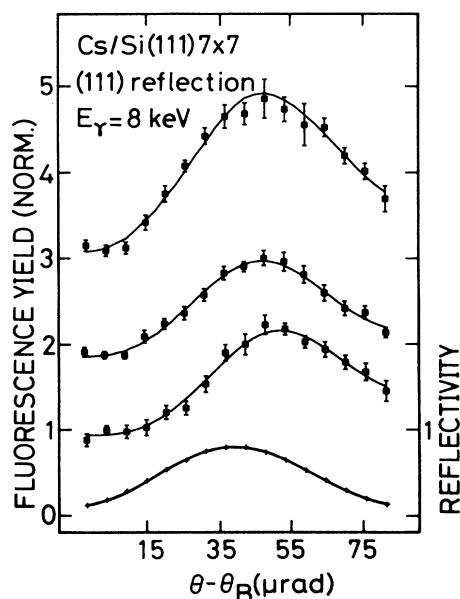
FIG. 3. Cs/Si(111)7×7, (111) reflection at 8.0-keV energy. Experimental data points and theoretical curves (all normalized) for the Cs L_a fluorescence yield ($\square$) and silicon (111) reflectivity (+) as a function of reflection angle. From bottom to top are reflectivity, Cs fluorescence after 300 s at 500 °C, plus 1 s at 600 °C (vertical offset $=1$), and plus 2 s at 600 °C (vertical offset $=2$). For details see Table I.
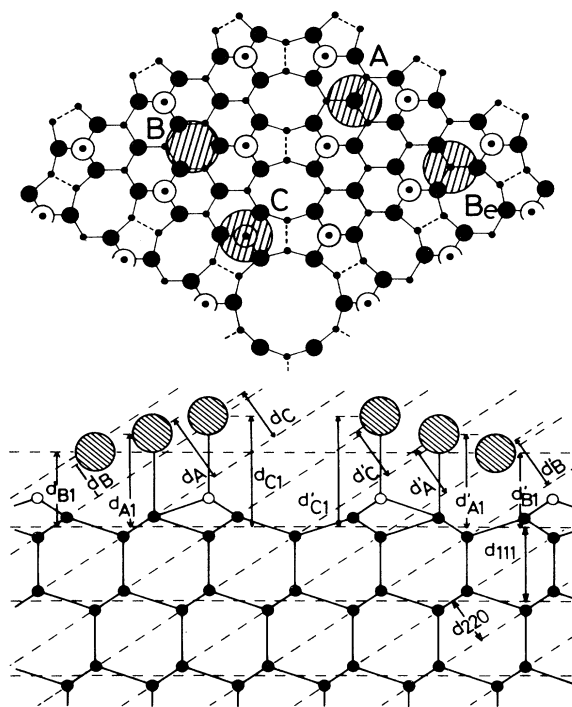

FIG. 4. Cs adsorption sites at the Si(111) surface (atomic sizes not at scale, solid circles: Si atoms; open circles: last-layer Si atoms; hatched circles: Cs atoms). Lower part: side view of the surface; upper part: top view of the surface. Adsorption sites: A, on-top site; B, threefold hollow site (normal); B_e, threefold hollow site in eclipsed position (not shown in the side view); C, adatom on-top site. Due to the stacking fault, two equivalent sites are possible for A and B adsorption sites. These equivalent sites have different distances to the [220] lattice plane.

types of site. In fact, taking into account the experimental phase and coherent fraction, a 42% of the Cs atoms should be at 3F sites, a 22% at on-top sites and a 36% at random sites (all values ±6%). The corresponding phase $\Phi_{(220)}$ agrees well with the expected value for B site (mean value of faulted and unfaulted halves). This fact does not contradict the (111) result. If B and A-type sites are simultaneously occupied, the expected $\Phi_{(220)}$ would be the mean value of the corresponding phases, considering the occupation of each site. Note, however, that the expected (220) phase difference between B site and A (unfaulted) site is close to 0.5. In this case destructive interference is produced,[13,14] and only the excess site is observed. Assuming the occupation obtained from $\Phi_{(111)}$, a $\Phi_{(220)}$ slightly over the experimental value should be observed (1.02). This suggests that the occupation of the unfaulted half is preferred, as these sites contribute to decrease the phase $\Phi_{(220)}$. The results for the annealed surface confirm this point (see following). The low coherent fraction observed in the (220) measurement is thus explained by the simultaneous occupation of several sites. Considering the (111) and (220) phase values, a significant occupation of C-type sites can be discarded, although a small number could be present. We conclude that for nonannealed layers, simultaneous occupation of A and B sites takes place. Magnusson and Reihl proposed the existence of two types of site for this system on the basis of their photoemission results,[9] although they could not identify them.

After annealing to 500 °C, we get a $\Phi_{(111)}$ value which nicely agrees with the corresponding one for 3F sites. Assuming that also on-top sites are still present, one would achieve a 52% of Cs atoms at 3F sites, a 9% at on-top

sites, and a 39% at random sites. The coherent phase $\Phi_{(220)}$ value reproduces quite well the expected phase Φ for the B site on the unfaulted half. The $f_{c,(111)}$ increases upon annealing, and the coherent coverage (0.07 ML) is close to the maximum coherent coverage possible for four Cs atoms per unit cell, adsorbed at the unfaulted half (0.08 ML). Thus, it is difficult to distinguish whether the faulting is released or only adsorption on the unfaulted half is favored, but the coherent coverage value indicates that partial adatom removal takes place. This fact could explain why the 3F sites are significantly more populated after annealing of the surface, which facilitates adatom

TABLE II. Expected positions (in units of lattice spacings).

Site	$d_{[111]}$	$d_{[220]}$ Unfaulted	Faulted	Mean
A [a]	1.24	1.49	1.16	1.33
B [b]	0.99	0.82	1.16	0.99
B_e [c]	0.99	1.49	1.49	1.49
C [d]	1.49	1.16	1.16	1.16

[a]A: on-top site.
[b]B: threefold hollow site (normal).
[c]B_e: threefold hollow site (eclipsed).
[d]C: adatom on-top site.

removal. Similar preferences (but for the faulted half) have been observed in the Li/Si(111) case.[10] In fact, the scanning tunneling microscopy results have shown several asymmetries in the electronic structure of Si(111)7×7.[20] In particular, an empty state is preferentially localized at the unfaulted half of the 7×7 unit cell.[20] As Cs atoms are expected to transfer charge into the empty states of the silicon surface, this fact could explain the observed preference. The good agreement between the experimental results and the model indicates that at the adsorption site no surface relaxation over ~0.2 Å takes place (with respect to the bulklike vertical positions of the topmost silicon layer excluding the adatoms). This value includes possible errors in the bond-length determination. We conclude that after the adlayer reordering, the B hollow site of normal type is preferred.

Subsequent annealing diminished the coverage to even smaller values (~0.07 ML). Under these conditions no (220) measurements could be performed due to the low counting rate obtained. The (111) measurements display a clear increase in phase as the coverage is further reduced. This increase is indicative of a change in the adatom-adatom and adatom-substrate interactions with respect to the saturation values, as was concluded from metastable deexcitation spectroscopy results.[7] The increase can be attributed to two possible reasons according to our analysis: occupation of a new type of site (which could be a defect site or a high-symmetry site); or a bond-length change [as was observed in the case of Cs/Ag(111) (Ref. 21)]. Occupation of defect sites contradicts the clear increase of f_c when the coverage is reduced, because this type of site usually contributes to the random fraction. Occupation of a new type of site (A site, to account for the phase increase) looks improbable in view of the fact that after the first annealing cycle the A sites were not occupied any longer, indicating a smaller bonding energy for A sites than for B sites, but it cannot be discarded. The remaining possibility is a bond-length change. If this were the case, a bond-length change from 3.5 to 3.8 Å when going from 0.14 to 0.07 ML would be taking place. The alkali-metal/silicon interface formation is characterized by a strong work function decrease as the coverage increases.[9] This decrease has been generally attributed to a coverage-dependent dipole moment per atom.[1] This means that either the charge transferred or the bond length (or both) are changing with the coverage, from a larger to a smaller value as the coverage increases. In short, the bond length would be affected by the transition from a covalentlike bond at high coverages to a more ioniclike bond at lower coverages.[1] Note that a bond-length change at coverages over 0.15–0.20 ML can be discarded in view of the values of the (111) and (220) phases.

V. CONCLUSIONS

The adsorption of Cs on Si(111) was investigated by using x-ray standing-wave fields. By employing two reflections [(111) and (220)], we were able to identify the Cs adsorption site as the hollow one of B type (threefold normal) after annealing of the surface and ordering of the adsorbate atoms. At room temperature on the contrary, a substantially disordered layer is obtained, with simultaneous occupation of on-top, threefold, and threefold (eclipsed) sites. At very low coverages a significant change in the (111) phase is measured. From this result it could not be uniquely discriminated between occupation of a new site or a bond-length change.

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