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Submonolayers of Lead on Silicon (111) Surfaces: An X-Ray Standing Wave Analysis

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1. INTRODUCTION

Systematic studies of adsorbed atoms on silicon surfaces have greatly contributed to our present understanding of the structures and the mechanisms of interface formation. In the case of the group III metals Al, Ga and In deposition of 1/3 monolayer (ML) on the Si(111) 7x7 surface produces a $\sqrt{3}\times\sqrt{3}$ R30° (denoted by $\sqrt{3}\times\sqrt{3}$ from now on) reconstruction. Although several models were proposed to explain this reconstruction, recent theoretical studies indicate /1/ that the eclipsed (T_4) model in which the metal atom is placed in the threefold-symmetric site above a second-layer Si atom has the lowest total energy if substrate relaxation is included and provides the best agreement with photoemission experiments. When group IV atoms are deposited on the Si(111) 7x7 surface several different superstructures (e.g., 5x5, 7x7, c(2x8), 1x1, $\sqrt{3}\times\sqrt{3}$) are found. By analogy with the group III metals it might be expected that the $\sqrt{3}\times\sqrt{3}$ structures produced by 1/3 ML Sn or Pb on Si(111) could be explained by the threefold eclipsed model. In the present study we have applied the x-ray standing wave (XSW) technique to the Si(111) $\sqrt{3}\times\sqrt{3}$-Pb system in order to determine the position of the Pb atoms relative to the bulk Si lattice.

The XSW technique makes use of the spatial periodicity and the phase tunability of standing wave fields. By making an XSW measurement with (hkl) substrate reflection one extracts the phase (Φ) relative to the substrate diffraction planes and the amplitude (f_c) of the (hkl) Fourier component of the adsorbate atom density distribution function. The phase is closely related to the distance of the adatoms from the surface in the [hkl] direction and the amplitude is related to the degree of order in the overlayer. The quantities Φ and f_c are obtained by a least-squares fit of the normalized fluorescence yield from the overlayer atoms with an expression derived from the dynamical theory of x-ray diffraction. Previously the method has been used successfully to determine the position of adatoms on surfaces /2-5/.

2. EXPERIMENT

The samples were prepared in the UHV photoemission system at the FLIPPER II beamline in HASYLAB /6/ and were subsequently transferred to the wiggler beamline in a small portable UHV chamber fitted with a 0.5 mm thick Be window. The XSW experimental set-up at the wiggler beamline has been described in Ref. /7/.

Proc. ICOSS-II, Amsterdam, June 1987, J.F. van der Veen and M.A. Van Hove (eds.), Springer Series in Surf. Scie.

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Clean Si(111) 7x7 surfaces were produced by heating to 950°C for 10 minutes and cooling slowly (< 50°/min). No impurities were detected by photoemission and clear sharp 7x7 LEED patterns were obtained. Pb was evaporated from a Knudsen cell at 0.4 ML/min onto the substrate either at RT or 250°C. The $\sqrt{3}\times\sqrt{3}$ reconstruction was obtained by subsequent annealing at 400°C as first described by ESTRUP and MORRISON /8/. Although the deposition rate was monitored with a quartz microbalance the final coverage was a little uncertain because Pb atoms were desorbed during annealing. A relative measure for this correction from Pb-desorption was obtained from the intensity of the Pb 5d core levels in photoemission. Similar desorption effects were observed by SAITOH et al. /9/.

3. RESULTS and DISCUSSIONS

The $\sqrt{3}\times\sqrt{3}$ R30° LEED pattern could originate from the atop, open or eclipsed site adsorption on Si(111) surfaces. At the atop site on a Si(111) surface an adatom is directly attached to a surface Si dangling bond. At the open site the adatom is at the threefold hollow position over a fourth layer Si atom and at the eclipsed site at the threefold position over a second layer Si atom. The adsorbate will have different density distributions if the atoms are at different adsorption sites and at different distances from the surface. This distribution is Fourier analyzed by the XSW method to determine the structure.

The results of XSW measurements on Si(111) $\sqrt{3}\times\sqrt{3}$-Pb deposited at RT with a (111) reflection are shown in Fig. 1, and those with a (220) reflection in Fig. 2. The phases (Φ) and amplitudes (f_c) of the Pb atom density distribution, can be interpreted in terms of the adsorption site(s) of Pb and Si-Pb bond length(s). This is relatively simple when the adsorbed atoms are at a single type of site. The analysis is more difficult for multisite adsorption. However, with reasonable assumptions even complicated structures can be solved /10,11/. No theoretical calculation, which could be taken as a guide, is hitherto available for the Pb/Si(111) system regarding the energetics and the Si-Pb bond lengths associated with different adsorption sites. However, noting the similarities between the LEED patterns of Pb on Si(111) and group III metals on Si(111) /12/ for a coverage of 1/3 ML, we can use some of the theoretical results available for the Al/Si(111) system /1,13/, with adjustments to account for the Pb atom. The Al/Si(111) system has been chosen because only for this system the largest number of adsorption sites has been compared within the same theoretical framework, and the preparation dependence of the LEED, photoemission and vibrational frequency data have been explained /13/. The estimated Si-Pb bond lengths, from the corresponding Si-Al bond lengths, the expected Φ values and the measured ones for different adsorption sites are listed in Table 1. For the set of data (a), obtained for RT deposition of Pb, good agreement with the atop site adsorption is seen from the table. This agreement also suggests the absence of any significant relaxation of the substrate. If one assumes an outward relaxation of 0.50 Å and assigns the Pb atoms at the eclipsed site, Φ(111) = 0.94 would be expected. However, in this case Φ(220) would be 1.41 - inconsistent with the observed value of 1.07. Assignment of the Pb atoms to the open site or the relaxed eclipsed site would also require an unreasonably large outward relaxation of 0.72 Å to explain the measured Φ(111). This would also produce Φ(220) values quite different from the one observed. Therefore, we conclude that for this preparation Pb atoms occupy the atop sites /14/. The small values of the amplitudes (f_c) in both (111) and (220) cases can be interpreted to be arising from the presence of a fraction of Pb atoms at nonpreferential positions. Disorder has also been observed for the Ge/Si(111) interface /11/. Presumably, the bond non-saturation in these systems leads to disorder. The model for the atop site adsorption is shown in Fig. 3 with the (111) and (220) distance components.

Table 1: Estimated Si-Pb bond lengths from theoretical Si-Al bond lengths for different adsorption sites, and the expected and measured phases of the (111) and (220) Fourier components of the Pb atom density distribution.

Adsorption site	Bond length Å Si-Al Theory[a]	 Si-Pb estimated*	Φ(111) expected	 measured	Φ(220) expected	 measured
atop	2.37	2.66	0.97[a] 0.96[c]	a)0.94±0.04 b)0.82±0.01	1.13[a] 1.12[c]	a)1.07±0.08
open	2.55	2.89	0.71[a][b] 0.58[c]		1.45[a] 1.27[c]	
eclipsed	2.68	3.02	0.78[a] 0.58[c]		1.20[a] 0.94[c]	
relaxed# eclipsed	2.44	2.78	0.71[a] 0.72[b]		1.11[a] 1.13[b]	

a) From Ref. 13 b) From Ref. 1

c) These values have been obtained by using the sum of the covalent radii or Pauling tetrahedral covalent radii for Pb and Si for the Si-Pb bond length. See Ref. 15.

* For the atop site: Si-Pb has been obtained by adding the difference of covalent radii (0.29 Å) of Al and Pb to the Si-Al bond length. For a threefold site the bonds are in general of more ionic character and, therefore, the difference between the ionic radii (0.34 Å) has been used.

\#. This relaxation basically involves vertical displacements of the second and third layer Si atoms and only lateral displacements of the first layer Si atoms. Atomic displacements in Ref. 1 are very similar to those in Ref. 13.

The quoted values of Φ in Table 1 is the average value and the error accounts for the variations observed for different samples and for different spots on the same sample. The high photon flux from the wiggler beam line allowed measurements on small spots of area ~0.2 mm^2. In some cases it was necessary to make measurements on very small spots, the spot size being limited to the available strainfree region of the crystal.

The results of XSW measurements for the sample prepared by deposition at 250°C are shown in curve b, Fig. 1. [No (220) measurement has been made corresponding to this preparation]. The observed Φ does not correspond to any of those expected for different adsorption sites (see Table 1). However, this phase (Φ= 0.82) can be seen to be due to the occupation of multiple sites. For example, if we assume 50 % of the Pb atoms at the atop site (Φ= 0.97) and 50 % at the open or relaxed eclipsed site (Φ= 0.71) the phase and amplitude of the Fourier component of this distribution would be Φ = 0.84 d_{111} and f_c = 0.68, respectively, which are very close to the observed values of Φ = 0.82±0.01 and f_c = 0.72±0.02. This corresponds to a situation where all the Pb atoms are in registration with the surface atoms, though at more than one preferential sites. As the observed Φ value is between the expected Φ values for the eclipsed and atop sites, it can also be explained by assuming a different population distribution at these two sites. This means that from our present data we cannot discriminate among the threefold sites. However, it is clear that we still need the atop component to explain these results.

As mentioned before, with the Pb atoms at the atop site fewer bonds are saturated. This could be part of the reason why high disorder (small f_c, f_c = 0.3) was observed for RT deposition. On the other hand, for the occupation of a threefold site, such as open, eclipsed or relaxed eclipsed, more bond saturation is expected, which could be responsible for a more ordered overlayer (large f_c). We observe a large f_c in the case of deposition at 250°C which can be explained in terms of coadsorption at the onefold atop and one or more of the aforementioned threefold sites. In fact, this set of data (Φ= 0.82, f_c = 0.72) can have another possible explanation. Since the expected Φ for the eclipsed site (Table 1) is very close to the observed Φ, one interpretation could be: 72 % of the Pb atoms are at the eclipsed sites and the rest in random distribution. However, in this case the substrate would be outwardly relaxed by 0.13±0.03 Å. Theoretical studies on the Pb/Si system could help to resolve these questions.

It should be noted that deposition of ~1 ML Pb at RT followed by heating at 300°C produces a $\sqrt{3}\times\sqrt{3}$ R30° LEED pattern (the so-called β-phase). Upon further heating at 400°C a second $\sqrt{3}\times\sqrt{3}$ R30° pattern appears (the so-called α-phase) corresponding to 1/3 ML of Pb, the rest of Pb being desorbed /8/. The Pb/Ge(111) system shows a similar behaviour. The observed phase value in the present study for the RT-deposited sample, Φ(111) = 0.94, is close to what we have observed for the β-phase of Pb/Ge(111) system, Φ(111) = 0.96 /16/. This indicates some structural similarity, at least in the distance component in the [111] direction, between the α- and the β-phase obtained by RT deposition followed by annealing.

4. CONCLUSIONS

We have shown that the $\sqrt{3}\times\sqrt{3}$ R30° LEED pattern obtained for 1/3 monolayer of Pb on Si(111)7x7 surface, corresponds to different geometrical arrangements of the adatoms depending on the sample preparation. Single site or multisite adsorption appears to be favoured under certain preparation conditions. This hints at the existence of more than one high symmetry adsorption sites with nearly equal binding energies of the Pb atoms.

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14. If we accept the lower limit of the measured Φ value, that is 0.90 (Table I), the expected values of 0.97 for the atop site and 0.71 for a threefold site would indicate that 31% of the ordered Pb atoms are in threefold site(s).
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Figure Captions

Fig. 1 Reflectivity (R) for the silicon (111) reflection: experiment (pluses), theory (dashed line), and Pb L_α fluorescence yield (Y): experiment (circles, squares), theory (solid lines), as a function of wavelength of the incident x-rays. $\Delta\lambda = (\lambda_B - \lambda)$ is the deviation from λ_B that satisfies the Bragg condition. The equivalent $\Delta\vartheta (= \vartheta - \vartheta_B)$ scale is shown at the top. Curves a and b correspond to deposition at RT and at 250°C, respectively.

Fig. 2 Meanings of the symbols are as in Fig. 1, but in this case for silicon (220) reflection.

Fig. 3 A Pb atom at the atop site with an Si-Pb bond length of 2.56 Å is shown. The distance components are measured from the diffraction planes as shown. Note that the (111) diffraction planes are halfway between the silicon bilayers.

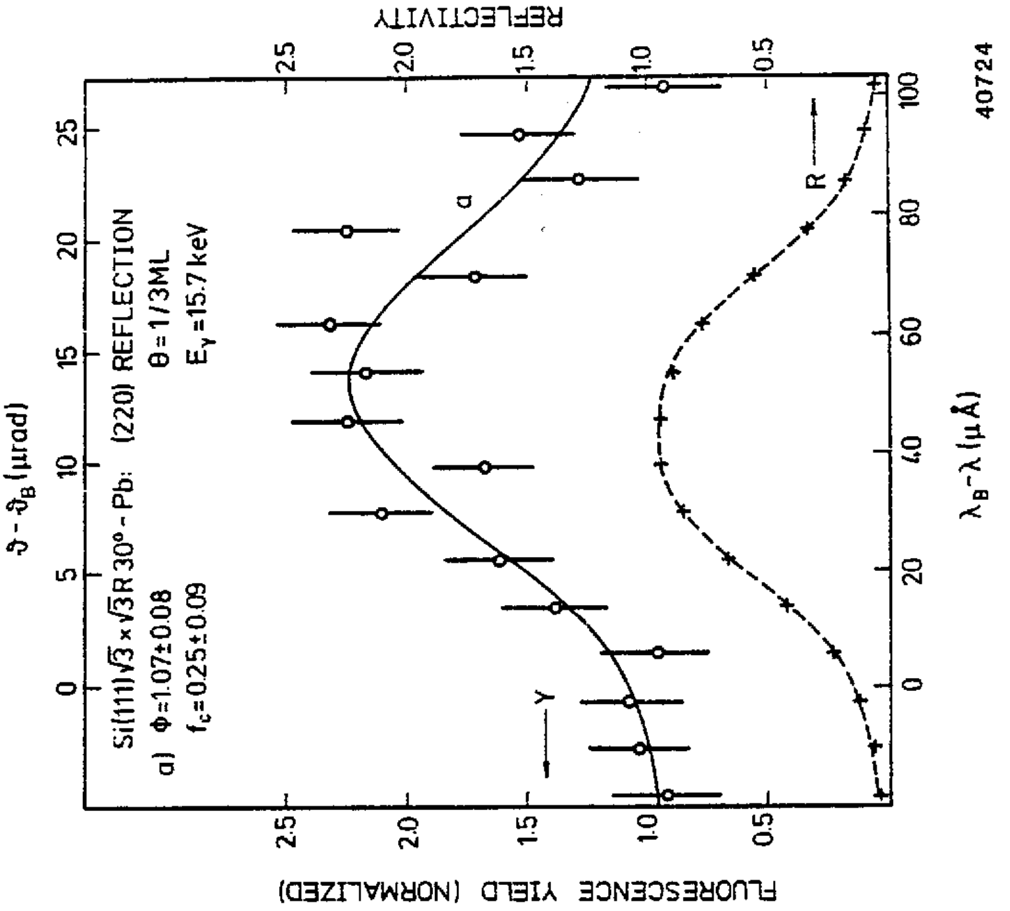
Si(111)√3×√3R30°-Pb: (220) REFLECTION
θ=1/3ML
E$_\gamma$=15.7keV
a) Φ=1.07±0.08
f$_c$=0.25±0.09
ϑ-ϑ$_B$(μrad)
0
5
10
15
20
25
REFLECTIVITY
2.5
2.0
1.5
1.0
0.5
FLUORESCENCE YIELD (NORMALIZED)
2.5
2.0
1.5
1.0
0.5
λ$_B$-λ(μÅ)
0
20
40
60
80
100
a
Y
R
40724

Fig. 2

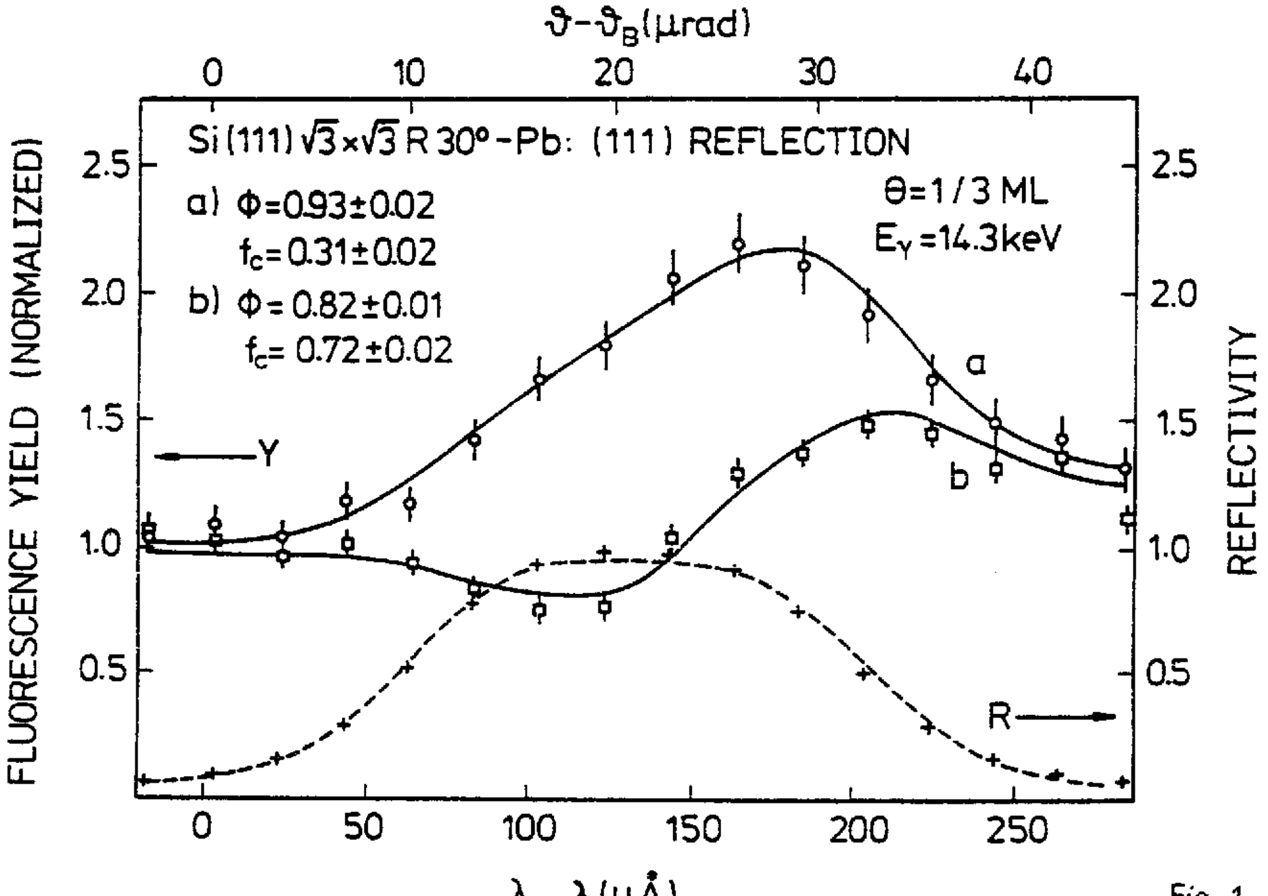
ϑ-ϑ$_B$(μrad)
0
10
20
30
40
Si(111)√3×√3R30°-Pb: (111) REFLECTION
a) Φ=0.93±0.02
f$_c$=0.31±0.02
b) Φ=0.82±0.01
f$_c$=0.72±0.02
θ=1/3 ML
E$_\gamma$=14.3keV
FLUORESCENCE YIELD (NORMALIZED)
2.5
2.0
1.5
1.0
0.5
REFLECTIVITY
2.5
2.0
1.5
1.0
0.5
Y
R
a
b
0
50
100
150
200
250
λ$_B$-λ(μÅ)

Fig. 1

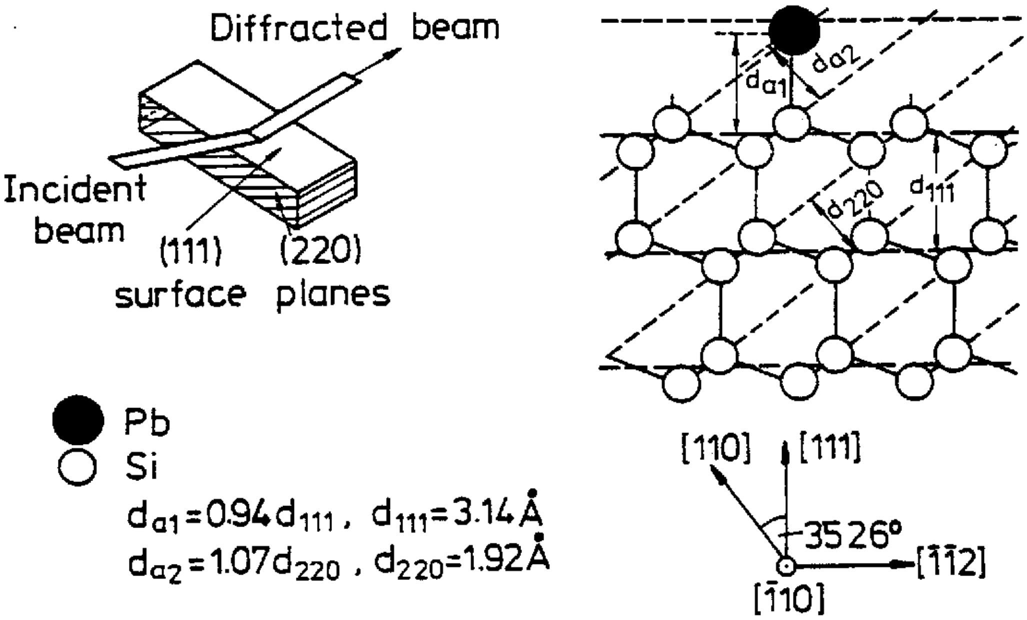
Diffracted beam
Incident beam
(111) surface
(220) planes
Pb
Si
$d_{a1}=0.94d_{111}$, $d_{111}=3.14$ Å
$d_{a2}=1.07d_{220}$, $d_{220}=1.92$ Å
d_{a1}
d_{a2}
d_{220}
d_{111}
[110]
[111]
35 26°
[$\bar{1}\bar{1}$2]
[$\bar{1}$10]

Fig. 3