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Evidence for valence-charge fluctuations in the $\sqrt{3}\times\sqrt{3}$-Pb/Si(111) system

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We have investigated the 1/3 monolayer $\sqrt{3}\times\sqrt{3}$-Pb/Si(111) system with core level photoemission at temperatures of 300 and 120 K. At both temperatures the Pb $5d_{5/2}$ and $5d_{3/2}$ core levels are split into two states with an intensity ratio of 2:1, as in the related Sn/Ge(111) and Sn/Si(111) systems. On doping the surface with Cs (an electron donor) or oxygen (an electron acceptor) the ratio of the intensities of the two states change strongly, suggesting the states have filled or empty dangling bonds. The results are interpreted in terms of charge fluctuations with one third of Pb atoms acting as charge donors and two thirds as acceptors in the undoped phase. Four chemically shifted Si $2p$ core level peaks are found whose energies are almost constant for the doped and undoped surfaces, and whose relative intensities change significantly on doping. These states of Si are assigned to two distinct kinds of atoms bonded to the two states of Pb, and to deeper Si atoms. The shifts are explained in the framework of the charge fluctuation model [M. Göthelid, M. Björkvist, T. M. Grehk, G. Le Lay, and U. O. Karlsson, Phys. Rev. B **52**, R14 352 (1995)], and the integer pseudo charge model [G. Ballabio, G. Profeta, S. de Gironcoli, S. Scandolo, G. E. Santoro, and E. Tosatti, Phys. Rev. Lett. **89**, 126803 (2002)]. Within the family of group IV metals adsorbed on group IV (111) semiconductor surfaces, Pb/Si(111) is similar to Pb/Ge(111) and Sn/Ge(111) with Sn/Si(111) being the exceptional case.

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I. INTRODUCTION

Considerable attention has recently been focused on the family of adsorption systems comprising group IV metals (Sn, Pb) on (111) surfaces of the group IV semiconductors Si and Ge.[1–4] Of particular interest are the properties of structures with 1/3 monolayer (ML) coverage of metal, known as the α phase for Sn systems and the β phase (for historical reasons) for Pb/Si(111); in these phases, the metal atom is located in the T_4 site. Alloys also form with the substrate atoms substituting metal atoms, for example, the γ (or mosaic) phase with 1/6 ML of metal and 1/6 ML of Si or Ge.

A notable feature of the Sn/Si(111), Pb/Ge(111), and Sn/Ge(111) systems is the existence of two core level states in photoemission with a relative intensity of 2 in the 1/3 ML$\sqrt{3}\times\sqrt{3}$ structure, even though the primitive unit cell contains only one metal atom, so that a single state should exist for this structure. On cooling, both Pb/Ge(111) and Sn/Ge(111) display a (3×3) structure, which has three metal atoms per unit cell, and is consistent with two states of the metal, with a relative intensity (low binding energy peak/high binding energy peak) of 2. Sn/Si(111) also shows two core level states but with the binding energies reversed (the higher rather than the lower binding energy peak is more intense); in addition a (3×3) phase has not been observed. An early model to explain the existence of two core level states and the phase transition was the fluctuating charge model,[5] which was followed by, among other theories, the hypothesis of a charge density wave.[2,3] This has been challenged by further experimental findings and many alternative explanations have been offered.[6] De Gironcoli *et al.*[7] have drawn attention to the importance of bonding between the metal and the pair of substrate atoms directly below the metal atom in determining the electronic structure. Their explanation for the observed phase transition was termed a "bond density wave."

Currently a widely accepted model for Sn/Si(111) and Sn/Ge(111) is that the metal atoms exist in two distinct charge states with different vertical heights above the surface.[4] The $(\sqrt{3}\times\sqrt{3})\rightarrow(3\times3)$ phase transition which occurs on cooling is considered to be displacive, with short range order still occurring in the $(\sqrt{3}\times\sqrt{3})$ phase, which gives rise to two distinct core level states in photoemission. The high temperature phase fluctuates on a time scale much faster than slow probes like scanning tunneling microscopy (STM) so that it is not possible to directly image this local order. There are still several open questions: for instance the Sn/Si system shows a reversal in the relative intensities of the core levels with respect to Sn/Ge, and it is not completely clear which of the two core levels corresponds to the "up" and "down" atoms. Also there is not yet consensus on why no phase transition occurs for Sn/Si(111)[8] in contrast to Sn/Ge(111) and Pb/Ge(111), although Pérez *et al.* have argued that it is due to differences in degree of phonon softening.[9]

Much less evidence is available for the corresponding Pb/Si(111)β phase but STM has shown that at low temperature, limited regions of (3×3) and other reconstructions appear.[10–12] Reflection high-energy electron diffraction (RHEED) studies have reported that (3×3) streaks appear on cooling,[12] but no well ordered phase has been observed by diffraction.

Recently Yuhara *et al.*[13] showed that the Pb 5*d* core level states can be fitted by two peaks with a relative intensity of 2. We have also reported a similar observation in a brief communication,[14] pointing out that the interpretation is equivocal as alternative explanations, such as the coexistence of more than one phase, are possible. A core level photoemission study of the β phase has been reported by Carlisle *et al.*[15] in which they did not consider the possibility of two Pb states, and of the mosaic phase by Karlsson *et al.*;[16] we return to their results below. It appears that the Pb/Si(111) system is similar to the other members of this family insofar as a splitting of the metal core levels occurs and there is some tendency towards (3×3) formation.

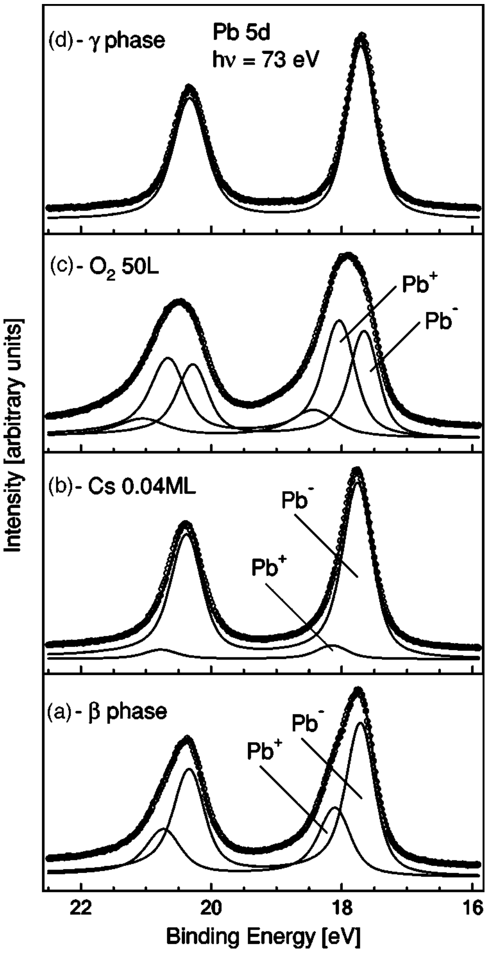

FIG. 1. Pb 5*d* core level, showing spin orbit split $5d_{3/2}$ and $5d_{5/2}$ components, normal emission. An integrating background has been subtracted from the raw data. Open circles: raw data; full lines: fitted curves. (a) β phase, (b) β phase after Cs doping, (c) β phase after O_2 doping, and (d) γ phase.

II. EXPERIMENT

We have investigated this system using core level photoemission and the method of doping pioneered by Le Lay and co-workers.[5,17] The measurements were carried out at the Czech Materials Science Beamline,[18] located at the Elettra Synchrotron Light Source, Trieste, Italy. The coverage of Pb was calibrated by evaporating several ML of Pb at room temperature onto a clean (7×7)-Si(111) surface, and then progressively evaporating off the Pb by annealing at constant temperature for fixed times. Carlisle *et al.*[15] have shown that the photoemission signal at saturation corresponds to a coverage of 1.3 ML; growth is by the Stranski-Krastanov mode, and excess Pb forms islands that do not contribute significantly to the photoemission signal. The Pb 5*d* and Si 2*p* signals were measured at photon energies (and resolution) of 73.0 (0.1) and 150.0 (0.18) eV, respectively. The PHOIBOS 150 hemispherical analyzer used has an angular acceptance of half cone angle 8°. We assume that the Pb 5*d* signal is linearly related to the coverage at fixed photon energy and angle of emission. The preparation conditions for the β phase were determined by correlating the low-energy electron diffraction (LEED) pattern with the Pb 5*d* intensity and the relative photoemission intensities of Pb and Si. Following Carlisle *et al.*,[15] the saturation coverage is calibrated to 1.3 ML. Then the β and γ phases should be observed when the photoemission intensity corresponds to coverages of 1/3 and 1/6 ML, respectively, and this did indeed occur. The Pb 5*d* lines were sharpest at a coverage of 1/6 ML or less, while a clear doublet was observed for 1/3 ML. The LEED

TABLE I. Pb line shape parameters resulting from fitting.

Pb				
Width of low BE component $=0.52\pm0.01$ eV Width of high BE component $=0.56\pm0.01$ eV			Spin-orbit splitting $=2.62\pm0.01$ eV	Branching ratio $=0.72\pm0.02$
Phase	Binding energy ±0.02 eV	Binding energy ±0.02 eV	Difference (eV)	Relative intensity (low BE peak/high BE peak)
β	18.11	17.72	0.39	2.0
β, Cs doped	18.15	17.76	0.39	12.6
β, oxygen doped	18.04	17.65	0.39	0.8

was checked and found to give the best $(\sqrt{3}\times\sqrt{3})$ patterns for these coverages.

Cs was dosed from a well outgassed SAES™ dispenser source. The coverage was calibrated by measuring the work function as well as the Cs 4*d* signal, and it was found that the shape of the work function curve was very similar to that of Cs on (7×7)-Si(111).[19] We assume that the coverage versus deposition time has the same shape and use the saturation value 0.4 ML to calibrate. The coverage was crosschecked by calculating the Cs 4*d* signal expected relative to the Pb 5*d* signal, using known values of cross section, and found to be consistent. For the evaporation time used in this study we found a coverage of 0.04 ML.

Oxygen was dosed at a pressure of 6.6×10^{-7} mbar for 100 s to give an exposure of about 50 L. As the sticking coefficient of oxygen on this surface is not known, we measured the intensity of the O 1*s* level, and the coverage was estimated to be 0.02–0.05 ML. This was quantified by comparing the intensity to that observed in previous experiments on Zr and Si (same experimental setup, signal normalized to flux).

Fitting was performed using the Igor® program with a line profile consisting of a convolution of a Doniach-Sunjic and Gaussian line shape for Pb, and a Voigt line shape for Si. The β phase is metallic while the mosaic phase is semiconducting, but the Doniach-Sunjic profile is used merely as a convenient choice for modeling asymmetric profiles, and we do not attempt to extract physically significant information from the line shape parameters. Both linear and integrating (Shirley type) backgrounds were tried and gave similar results with small changes in fit parameters that were not considered physically significant.

To ensure consistency, we fitted the pairs of spectra simultaneously. This was done by constraining the fit routine to apply the same parameters to both spectra and optimize the fit accordingly. For pairs of spectra taken at different angles of emission (normal and grazing) all parameters (binding energies, branching ratio, spin orbit splitting, and Voigt line shape) except the relative intensities were constrained to be the same. For pairs of spectra that were doped and undoped, only small binding energy shifts were permitted (usually 20 meV, with 110 meV for one peak on Cs doping) while the peak shapes were constrained to be the same for both spectra.

III. RESULTS

In Fig. 1 we show a comparison between the Pb 5*d* core level spectra of the β phase (1/3 ML), and the same surface doped with either 50 L of oxygen or 0.04 ML of Cs. A spectrum of the 1/6 ML Pb+1/6 ML Si γ (or mosaic) phase[20] is also shown for reference, but detailed results will be reported elsewhere. The spectra have been aligned with respect to the top of the valence band to eliminate effects due to surface band bending after adsorption of the dopant. The Pb 5*d* core level has a clearly asymmetric line shape in the β phase, which becomes slightly sharper after cooling from 300 to 120 K, but is symmetric and narrow in the mosaic phase. The β phase spectrum can be fitted by two slightly asymmetric spin-orbit split doublets with a relative intensity of 2, and slightly different widths and asymmetries, Table I. We label the low and high binding energy states Pb^- and Pb^+, respectively.

On doping with 0.04 ML of Cs, the spectral envelope became much narrower, and the spectrum was fitted again with two peaks with the same line shape parameters as previously except that one peak was very weak. The Pb^+ state was strongly reduced and the Pb^- peak became more intense (relative intensity 12.6). Conversely, on doping with oxygen, the spectral weight shifted to the Pb^+ state, and the $\mathrm{Pb}^-/\mathrm{Pb}^+$ relative intensity was 0.8 instead of 2.0 (see Table I). The binding energies and intensities were optimized for individual spectra (without simultaneous fitting) to test for consistency. The binding energies changed by only a very small amount, +40 for the Cs doped surface, and −70 meV for the oxygen doped surface, demonstrating that the main effect is transfer of spectral weight from one peak to the other, rather than a continuous peak shift.

For oxygen adsorption we also identified a broad, higher binding energy state at 18.44 eV binding energy which is assigned to direct bonding between Pb and oxygen atoms. This has an intensity of 14% of the total Pb intensity, amounting to about 5% of 1 ML. The presence of such a peak for oxygen but not for Cs can be understood in terms of the different atomic sizes (metallic diameter of Cs, 5.3 Å; covalent diameter of O, about 1.2 Å) and the strong affinity of oxygen for Si and Pb. Oxygen is evidently able to penetrate between the surface Pb atoms and bond directly to Pb or Si, whereas Cs probably remains above the surface. Similar results were obtained by doping at 120 K and room tem-

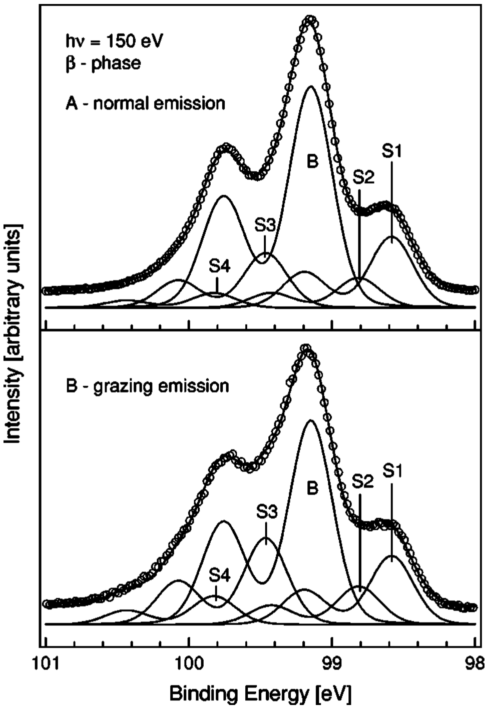

FIG. 2. β phase: Si $2p$, 300 K, after subtraction of an integrating background. Open circles: raw data; full lines: fitted curves.

perature. At low temperature diffusion is reduced, so the similarity of the behavior is an indication that the effects are due to long range doping effects, rather than local chemical interaction involving diffusion and rearrangement of the atomic structure.

Figure 1(d) shows that the Pb core level in the mosaic phase (in which the surface has a composition of 1/6 ML of Pb and 1/6 ML of Si) consists of a single state, namely the Pb^- state. This is consistent with STM results[20] which indicate charge transfer from Si to Pb.

The Si $2p$ core levels were also investigated: spectra were taken at both normal and 60° emission and the core levels were fitted as described earlier. The results for the undoped β phase are shown in Fig. 2. Comparing the normal emission spectrum, Fig. 2(a), and the more surface sensitive Si $2p$ spectrum, Fig. 2(b), there is a marked increase on the high binding energy side for the more surface sensitive geometry, and a lesser change on the lower binding energy side. It was not possible to fit the spectra using only three doublets, as was done by Carlisle *et al.*[15] Instead we found it was necessary to use five doublets to obtain an adequate residual curve (difference between fit and data). This is partly because of our higher resolution, and partly because we have a much more extensive data set, with variations in angle and doping. For example, in some cases it was possible to fit data from a single angle with a lesser number of peaks, but then the other angle of emission was not reproduced well.

The spectra also suggest the existence of five peaks, Fig. 2. The bulk peak gives rise to the strongest feature, and the intensity at lower binding energy labeled S1 is the most obvious surface peak. However at grazing emission the filling of the minimum between the bulk peak and S1 cannot be modeled by a single peak of constant width, so it is necessary to add a second peak, S2. Similarly the minimum between the spin orbit split components of the bulk peak is filled at grazing emission, implying the existence of a surface component around this energy, labeled S3. Last, the change of shape of the tail of the spectrum implies a fourth surface peak, S4.

The parameters of the bulk peak (B) and the four surface peaks are summarized in Table II. At 60° emission, peaks S2 and S3 increase in intensity by an average of 60% relative to the bulk peak intensity, S4 increases by 100%, while peak S1 increases by only 6%. Clearly S1 is associated with Si atoms that lie deeper in the surface than the others. The ratios of the intensity of S3 to S2 are 2 ± 0.2 at both normal and grazing emission.

On doping with Cs, Fig. 3(a), the same binding energies are found to within 20 meV except for S1, which shifts by 0.11 eV to −0.45 eV. States S3 and S1 are more intense while S2 is weakened. S4 retains the same relative intensity. Vice versa, oxygen enhances state S2 and weakens state S1 [see Fig. 3(b)]; S3 has about the same intensity relative to the bulk peak as for normal emission from the β phase, and S4 appears to be slightly stronger. As in the case of the Pb $5d$ core level, there is an extra peak S5 in the spectrum (with an intensity of 5% of the total intensity) which is assigned to direct bonding of oxygen to Si. This state is not considered further here.

TABLE II. Si line shape parameters resulting from fitting.

Si				
Width =0.35 eV	Spin-orbit splitting =0.61 eV		Branching ratio =0.52	
Phase, state and emission angle	Binding energy relative to bulk peak/ intensity relative to bulk peak intensity, ±0.02 eV			
	S1	S2	S3	S4
β, normal emission	−0.56 eV/0.32	−0.33 eV/0.13	0.32 eV/0.25	0.68 eV/0.07
β, grazing emission	−0.56 eV/0.34	−0.33 eV/0.19	0.32 eV/0.42	0.68 eV/0.14
β, Cs doped, normal emission	−0.45 eV/0.36	−0.31 eV/0.09	0.30 eV/0.28	0.67 eV/0.08
β, Cs doped, grazing emission	−0.45 eV/0.49	−0.31 eV/0.14	0.30 eV/0.50	0.67 eV/0.15
β, oxygen doped, normal emission	−0.57 eV/0.22	−0.32 eV/0.23	0.29 eV/0.24	0.62 eV/0.11
β, oxygen doped, grazing emission	−0.57 eV/0.23	−0.32 eV/0.35	0.29 eV/0.32	0.62 eV/0.17

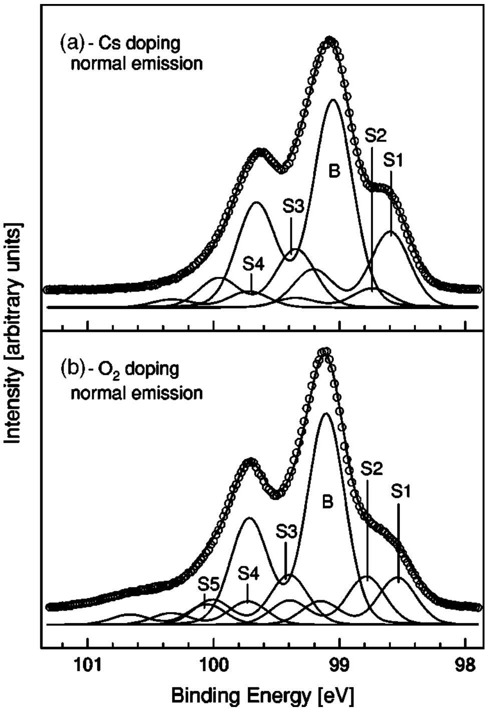

FIG. 3. Si 2*p* core level spectra. An integrating background has been subtracted from the raw data. Open circles: raw data; full lines: fitted curves. (a) Cs doped β phase, and (b) oxygen doped β phase.

LEED was also performed and we found that on cooling below room temperature, the $\sqrt{3}\times\sqrt{3}$ phase developed rather diffuse extra spots corresponding to (3×3) symmetry. This confirms earlier studies with RHEED[12] that showed streaks, but to our knowledge a (3×3) pattern has not been previously observed with LEED. In STM, various reconstructions have been observed, including the (3×3) phase, but over limited areas only. On doping with oxygen the LEED pattern became even more diffuse, but the extra spots did not disappear completely. This is consistent with the fact that doping with oxygen does not fully convert all the Pb$^-$ atoms to the Pb$^+$ state, but only changes the relative intensities.

IV. DISCUSSION

We interpret the core levels in terms of the schematic model shown in Fig. 4. As outlined earlier, there are two distinct states of Pb in the first layer, Pb$^-$ and Pb$^+$, with two Pb$^-$ atoms and one Pb$^+$ atom per (3×3) unit cell. The β phase structure contains a second layer of Si atoms in two chemically different states (considering only nearest and next nearest neighbors): those bonded to Pb$^-$ atoms (6 atoms per unit cell, light gray circles) and those bonded to Pb$^+$ atoms (3 atoms per unit cell, dark gray circles). The third layer consists of Si atoms in three states: those bonded to two "light" and one "dark" first layer Si atom (6 atoms per unit cell); and those directly under the Pb$^+$ atoms (1 atom per unit cell) or Pb$^-$ atom (2 atoms per unit cell)—these are not visible in the top view drawing.

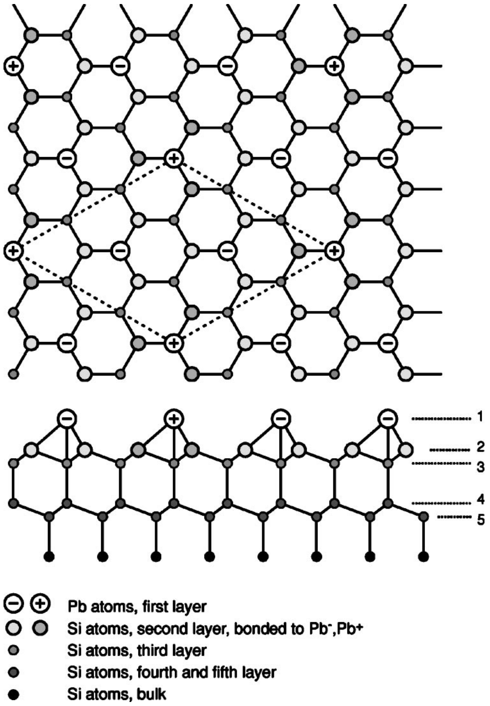

FIG. 4. Schematic diagram of the β phase. Top: plan view; bottom: side view. The (3×3) unit cell is indicated by a dashed line in the plan view. The second layer Si atoms underneath each Pb atom are shown connected by a line to the Pb atoms in the side view.

The surface sensitive peaks S3 and S2 have a relative intensity close to 2 for the β phase so we assign them to second layer Si atoms bonded to Pb$^-$ (S3) and Pb$^+$ (S2) atoms. The Si core level shifts are in the opposite direction with respect to the Pb$^-$ and Pb$^+$ core level components, so within an initial state picture of chemical shifts it is natural to consider these Si atoms as charge donors (S3 to Pb$^-$), or acceptors (S2 from Pb$^+$), in relation to the Pb atoms. This assignment is qualitatively consistent with the doping experiments: on doping with Cs, the intensity of S2 decreases relative to S3 (as does Pb$^+$ in the Pb core level spectrum) while on doping with oxygen, S2 increases.

We assign the most surface sensitive peak S4 to defects in the top layer, for example, step atoms, or those bonded to residual contamination.

Peak S1 changes in intensity by very little between the surface and bulk sensitive geometries for the clean β and the oxygen doped phase, Table I, and so we assign it to deeper Si atoms. Our tentative assignment is to the Si atoms located directly under the Pb$^-$ atoms in the third and fourth layers, as well as to the same Si atoms under Si defects. According to the calculations of Gironcoli *et al.*[7] the third and fourth layer Si atoms are involved in bonding with the surface atoms, with the wave function of the metal induced surface state having a significant density between them. This assignment corresponds to 4 atoms per unit (3×3) cell, whereas the S3 state corresponds to 6 atoms per unit cell, but has lower intensity.

On doping with Cs, the intensity of the S1 state relative to the bulk increases, and on doping with oxygen it decreases, but the changes do not quantitatively reflect the changes in the intensities of the Pb states. The core level shift suggests these atoms are negatively charged, and thus doping changes the charge state of these third/fourth layer atoms. The lack of quantitative agreement may indicate that other Si atoms also contribute to this peak. While other core levels appear to change only their intensity, the S1 state behaves slightly differently on Cs doping. It becomes more surface sensitive and shows an anomalously large shift of 0.11 eV, compared with a maximum of 0.02 eV for S2, S3, and S4. This is an indication that this peak may also contain another contribution in the case of Cs doping.

In previous studies, Carlisle *et al.*[15] fitted the β phase Si core level spectrum with a single low binding energy peak labeled P2 (corresponding to our peaks S1 and S2), and a high binding energy peak P1 (corresponding to our peaks S3 and S4). These were assigned to second layer Si atoms bonded to Pb (P2) and third layer Si atoms (P1). Our assignment is different and takes account of the fact that there are two states of Pb present.

An initial state model implies the lower binding energy peak is a state in which the Pb is more negatively charged, that is, the dangling bond is filled, whereas the higher binding energy state corresponds to Pb with an empty dangling bond. Obviously final state effects may also play an important role, but the observation of Pb core levels with an intensity ratio of 2, and Si core levels with a ratio of 0.5, strongly suggests that an initial state model is adequate to describe this system. The changes on doping, are also qualitatively consistent with this initial state model. Final state effects can always affect results so that the Pb^+ and Pb^- states may be better labeled as Pb(up) and Pb(down), but the present model explains an extensive data set with few assumptions.

The simultaneous existence of two charge states of Pb and of the underlying Si atoms, and a $\sqrt{3}\times\sqrt{3}$ LEED pattern, confirms that this system in the same class as Pb/Ge, Sn/Si, and Sn/Ge for (111) surfaces. The anomalous member of this group is Sn/Si(111), as the intensities of the core level lines are reversed, and it shows no indication of a (3×3) structure at low temperature. The doping experiments show that the core level shifts for both Pb and Si are initial state effects and unlikely to be due to final state (screening) effects. Furthermore, the near constancy of the binding energy in this wide range of data, and the fact that primarily intensity changes, supports the “pseudo integer charge” hypothesis of Ballabio *et al.*[21] The Pb surface atoms switch from one binding energy to another, and do not adopt intermediate chemical states in the β, Cs doped, and oxygen doped systems. Concomitantly, the underlying silicon atoms switch, with only very minor changes in binding energy. In this context the charge transfer is not defined in the ionic sense of complete transfer of an electron from one atom to another, but refers to the localization of an occupied state that may be nearer a Pb or Si atom.

As noted in Sec. I the method in these experiments was inspired by the results of Göthelid *et al.*[5] who studied doping of Sn/Si(111) and Sn/Ge(111). In the first study, much larger coverages of alkali metal (up to 1/3 ML) were used, while in the second study the doses were more similar to those used here (0.04–0.11 ML), but the effects on the metal line shape were dramatic and similar to those observed here. An alkali metal, potassium, suppressed the high binding metal energy state while an electronegative dopant, iodine, increased its intensity as in the present work. These authors noted an increased width of the Si core level for the undoped surface and assigned it to the existence of two different Si states influenced by the two Sn states. It is then natural to expect that these two states of Si can be resolved (as the metal core levels are) given suitable circumstances, and we believe that our study of Pb/Si(111) provides this favorable case, in terms of the system studied, the experimental resolution available and the use of two angles of emission.

V. CONCLUSIONS

In summary, on the basis of Si 2*p* and Pb 5*d* core level photoemission spectra, we have shown that the β phase of Pb/Si(111) is a fluctuating charge system, similar to Pb and Sn adsorbed on Ge(111) or Sn adsorbed on Si(111). Within this family the Sn/Si(111) is the anomalous member as no (3×3) low temperature phase is observed, and the relative intensity of the Sn core levels is reversed. Two states of Pb, labeled as Pb^- and Pb^+, exist with a stoichiometric ratio of 2:1. On doping with Cs the Pb atoms can be almost completely converted to the low binding energy state, while on doping with oxygen the stoichiometric ratio can be changed to about 0.8:1. The Si core level spectra indicate that bonding involves at least the third and fourth layer Si atoms. The spectral changes on doping, in which intensities of states change rather than binding energies, indicate that these results are consistent with the model of Ballabio *et al.*[21] in which an integral pseudo charge exists on the surface metal atoms.

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