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Core-level photoemission study of the Pb overlayers on Si(001)

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High-resolution core-level photoemission spectroscopy using synchrotron radiation and low-energy electron diffraction have been applied to study the intriguing structures of the Pb overlayers on Si(001) up to a coverage of 1 monolayer (ML). At a coverage of less than 0.6 ML, two distinct components are observed in Pb $5d$ core levels. This suggests that the Pb chains formed at this coverage range, as observed in the previous scanning tunneling microscopy studies, are composed of *buckled* Pb dimers consistent with the recent structure model. The Pb $5d$ core-level shift due to this buckling is measured to be 0.35 eV. The spectral line shape of Pb $5d$ at an intermediate coverage around 0.75 ML, exhibiting the $c(8\times4)$ phase in the low-energy electron diffraction, differs significantly from that of the lower coverages in contradiction to the available structure models with asymmetric buckled dimers. In contrast, the 2×1-Pb surface developed at a full monolayer coverage exhibits only single component in Pb $5d$. This result is compatible only with the close-packed *symmetric* dimer model. The spectral line shape of Pb $5d$ suggests a gradual change from a semiconducting to a metallic surface at 0.75–1.0 ML, which agrees with the previous valence-band photoemission study indicating the metallic nature of the 2×1 phase. Detailed analyses of the Si $2p$ core levels for the well-ordered 2×2, $c(8\times4)$, and 2×1 phases at 0.5, 0.75, and 1.0 ML, respectively, are given for the discussion of the Pb-induced Si surface reconstructions.

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I. INTRODUCTION

During the past decade there has been a significant amount of research in studying the fundamental physical and chemical processes in an atomic scale of the epitaxial growth of group-IV elements on Si surfaces, for example, Si/Si[1–3] Ge/Si,[4,5] Sn/Si,[6] and Pb/Si.[7–15] The former two systems provide model systems for the homo- and heteroepitaxial growth on semiconductor surfaces, respectively, and the latter systems, especially the Pb/Si system,[7] were discussed as one of the model metal/semiconductor interface systems with negligible solubility, i.e., with an abrupt interface. Recently, very exotic behaviors of the Pb/Si(111) system have been under focus, such as the formation of Pb quantum islands of unusual shapes[8] and the surfactant behavior for the fractal growth of Ge two-dimensional (2D) islands.[9] Such intriguing behaviors are thought to be closely related to the details of the atomic and electronic structures of the first monolayer (wetting layer) Pb on Si surfaces.[8] The Pb initial growth on Si(001) has received relatively little attention compared to the Pb/Si(111) system. However, recent scanning tunneling microscopy (STM) studies have revealed interesting and intriguing initial growth behaviors of Pb on the Si(001)2×1 surface.[10–14]

Pb has been known to grow in a layer-by-layer way up to a critical coverage of ~2.5 ML [1 monolayer (ML)$=6.8\times10^{14}$ atoms/cm^2] (three layers) at room temperature (RT), exhibiting a series of ordered surface phases.[15] During the formation of the first Pb layer on the surface, the Pb adsorbates exhibit a very anisotropic growth pattern, which leads to the formation of well-ordered and often very long one-dimensional adsorbate chains.[10–14] At a coverage of 0.5 ML these chains form a close-packed structure of a 2×2 periodicity. This one-dimensional growth feature is very similar to those of the group-III element adsorption (Al, In, and Ga) on Si(001), for which the adsorbate chains are composed of *symmetric* ad-dimers *parallel* to the chains and to the substrate Si dimers [Fig. 1(a)].[16–21] However, very recent STM (Refs. 11 and 14) and theoretical studies[12] have proposed the possibility of Pb dimer buckling within the adsorbate chains in contrast to the group-III cases [Fig. 1(b)]. However, no detailed structural studies for this unique structure proposed have been reported.

In further contrast to the well-studied group-III/Si(001) systems, the initial 2D layer growth of Pb proceeds beyond the 2×2 phase at 0.5 ML to form a complex $c(8\times4)$ structure at ~0.7 ML and a 2×1 phase at ~1 ML.[10,11,13,15] The first Pb layer was shown to saturate at ~1 ML, and further the second and third Pb layers grow in a layer-by-layer fashion.[10,11,15] Although there have been a few studies, mainly on the $c(8\times4)$ phase,[11,13] the atomic structures of these high-coverage phases and layers are largely uncertain yet.

In this paper, we report on a high-resolution core-level photoemission study for the Pb overlayers on the Si(001)2×1 surface for the 2D growth regime up to 1.0 ML. The evolution of the Pb $5d$ and Si $2p$ core-level line shapes is carefully investigated along with that of the low-energy electron diffraction (LEED) patterns. From the observed core-level shifts, we critically review the structure models proposed so far and discuss the electronic property of the surfaces.

II. EXPERIMENT

High-resolution core-level photoemission measurements using synchrotron radiation was carried out at the newly built

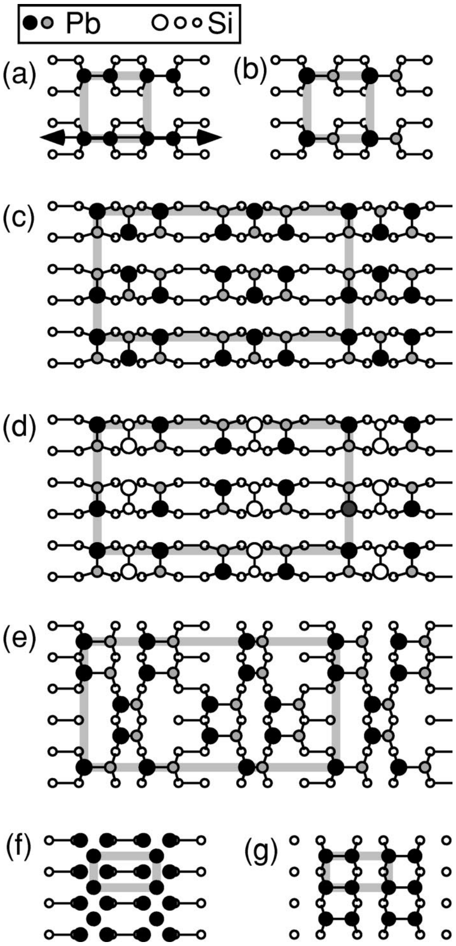

FIG. 1. Schematics of the structural models for (a) the Si(001)2×2-Al(-Ga and -In) surface, (Refs. 16–21), (b) the Si(001)2×2-Pb surface at 0.5 ML (Refs. 11, 12, and 14), (c)–(e) the Si(001)$c(8\times4)$-Pb surface at (c) 0.75 ML (Ref. 13), (d) 0.5 ML (Ref. 13), and (e) 0.75 ML (Ref. 11), respectively, and (f, g) the Si(001)2×1-Pb surface proposed by (f) surface x-ray diffraction (Ref. 32) and (g) STM (Ref. 11) studies, respectively. The surface unit cells are indicated by thick gray rectangles and the arrow in (a) indicates the 1D adsorbate chain direction.

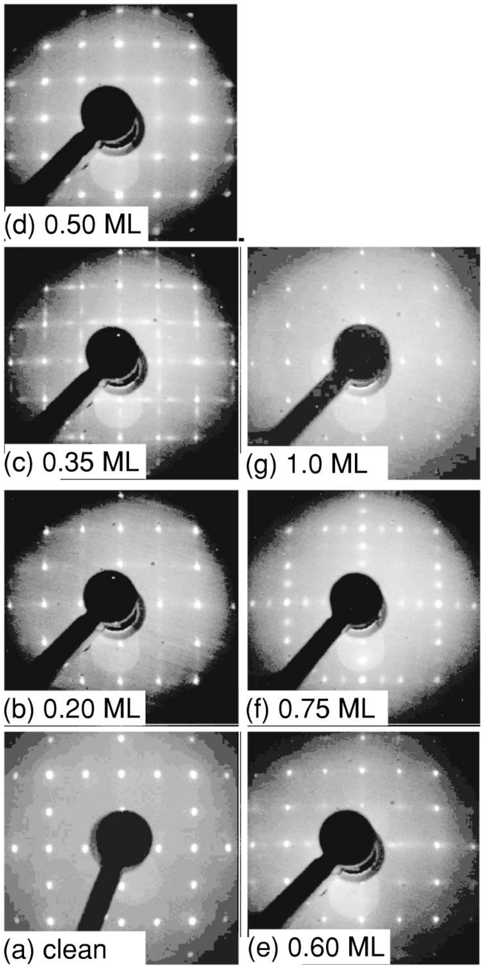

FIG. 2. LEED patterns observed during Pb deposition on Si(001)2×1 at room temperature with different Pb coverages as indicated.

high-resolution vacuum ultraviolet beam line BL-1C of Photon Factory, KEK. The photon energy range covered is from 20 to 250 eV using a varied-line-spacing grating monochromater with a nominal spectral resolving power better than 10 000. The end station of this beam line is equipped with an angle-resolved photoelectron spectrometer system (Vacuum Generator, ARUPS 10) with a full multichannel dectector system and a LEED optics.[22] The base pressure of the ultrahigh vacuum chamber for measurements was better than 2×10^{-10} Torr. The angle of the incident photon beam was kept at 45° from the normal to the sample surface. The total energy resolution was better than 75 meV for all photon energies used and the angular resolution of analyzer was set to 2°. An *n*-type Si(001) wafer was cleaned *in situ* by resistive heating up to ~950 °C and flashing at ~1200 °C for a few seconds, which gave rise to a sharp double-domain 2×1 LEED pattern [see Fig. 2(a)]. Pb was deposited onto the Si(001)2×1 surface kept at RT from a well-degassed Knudsen cell.[23] The evaporating rate was measured by a quartz microbalance and the coverage was calibrated by the sharp 2×2 LEED pattern as 0.5 ML. The estimated uncertainty of the coverage in this way is less than ±0.05 ML. The pressure was less than 8.0×10^{-10} Torr during the Pb deposition. Curve fitting of the core-level spectra was carried out by a standard least-square fitting procedure utilizing a set of spin-orbit doublets in Voigt or Doniach-Sunjic function forms.[21,24]

III. RESULTS AND DISCUSSION

In Fig. 2, the LEED patterns are shown for Pb coverages up to 1.0 ML. We observed $\times2$ streaky lines in the coverage range of 0.2–0.4 ML [Figs. 2(b) and 2(c)]. At the coverage of ~0.35 ML the streaks appear more or less as a diffuse double-domain 2×3 pattern [Fig. 2(c)]. The streaks and the 2×3 pattern are very similar to those of the Al and In adsorption on Si(001)2×1 in a similar coverage range.[19,20] As clearly shown in the STM studies[10,11,13,14] in this coverage range the Pb adsorbates [or Al, In, Ga (Refs. 16 and 19) and Sn (Ref. 6)] form one-dimensional adsorbate chains, which are perpendicular to the substrate Si dimer rows. There is now a well-established consensus that the chains due to Al, Ga, and In are composed of the *parallel dimer* structures, where the metal adsorbates form symmetric dimers in parallel to the substrate Si dimers [Fig. 1(a)].[17,18,20] Then the streaks and the 2×3 pattern indicate that these chains have certain interchain interaction to form a long-range ordering in their interchain distance, that is $3a_0$ for the fully developed 2×3 phase at $\frac{1}{3}$ ML (more generally a $2\times n$ phase).[19] The 2×3 ordering was previously observed for Al, Ga, and In adsorbates but only after a mild annealing at 100–300 °C.[19] The formation of a 2×3 phase at RT for Pb adsorbates then suggests that the interchain interaction, possibly a repulsive interaction, is stronger for the Pb dimer chains. On the other hand, the Pb chains could be more mobile than the group-III chains. The origin of such interchain interaction has not been clarified yet. Other than the streaks and the 2×3 pattern, the evolution of the LEED patterns is consistent to the previous LEED studies: As the coverage is increased, the 2×2, $c(8\times4)$, and 2×1 phases are observed at 0.50, 0.75, and 1.0 ML, respectively (Fig. 2).[10,11,15,23] These structures will be discussed in detail based on the Pb $5d$ and Si $2p$ core-level data.

Pb $5d$ core-level spectra were measured with a photon energy ($h\nu$) of 50 eV, as shown in Fig. 3, for the coverages corresponding to the different LEED patterns of Fig. 2. In raw data, with a large spin-orbit splitting of ~2.5 eV between the $5d_{5/2}$ and $5d_{3/2}$ components, one can easily see that the spectral line shapes are almost the same up to ~0.6 ML and then change to become sharper with increasing the coverage. The very blunt peak-top shape and the barely visible shoulders (see the vertical line of Fig. 3) of the spectra at 0.2–0.6 ML suggests that the Pb $5d$ spectra consist of more than one component. Furthermore, it is straightforwardly expected that the local structures of the Pb adsorbates are essentially unchanged up to ~0.6 ML but the structures change from 0.60 to 1.0 ML.

More detailed information is obtained by the curve-fitting analyses.[21,24] An integral or polynomial background was used and the Lorentzian width was optimized to be 0.37 eV. The branching ratio is 0.65 for 0.10–0.60 ML, 0.61 for 0.75 ML, and 0.58 for 1.0 ML. The difference in branching ratio is though to be due to a combined initial- and final-state effect, which is also affected by photoelectron diffraction in an angle-resolved measurement as in the present case.[25] The results of such curve fittings are also presented in Fig. 3. As suggested above, the Pb $5d$ spectra are found to consist of two components (denoted as P_1 and P_2) at coverages less than 0.6 ML, which clearly indicates at least two different adsorption sites with distinct chemical and structural environment. The splitting of P_1 and P_2 is determined to be 0.35 eV. We also found that these two components have roughly the same spectral intensity. This clearly means that the two kinds of Pb adsorption species are almost equally populated throughout that coverage range.

The above result rules out the possibility of the symmetric parallel dimer model in Fig. 1(a) which has been established for the group-III metal adsorbates but has a unique adsorption site.[17,18] The Al $2p$ and In $4d$ core-level spectra of these symmetric parallel dimers were shown to consist of a well-defined single component.[21] On the other hand, the observed splitting of the Pb $5d$ core levels can easily be explained by the *buckling* of Pb dimers within the parallel dimer structure [Fig. 1(b)], where the up- and down-dimer atoms have different local structures and different local valence-electron density of states. Such a buckled (asymmetric) parallel dimer model was indeed found to be the most energetically favorable configuration through an *ab initio* total-energy calculation.[12] The buckling is mainly due to an unsaturated, "dangling," bond on each Pb dimer atom, which tends to cause intradimer charge transfer from a dimer atom to the other. This situation is analogous to the well-known buckling of Si and Ge dimers on the clean Si(001) and Ge(001) surfaces.[24,26–29]

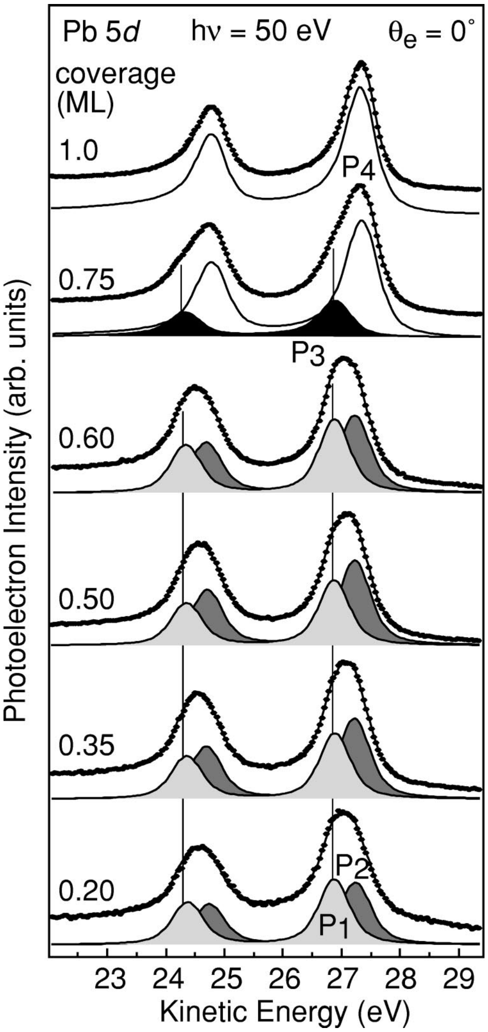

FIG. 3. A series of Pb $5d$ core-level spectra taken at a photon energy ($h\nu$) of 50 eV from the Pb/Si(001) surfaces corresponding to the Pb coverages indicated and to the LEED patterns in Fig. 2. Experimental data (dots) are superimposed with the results of the least-square curve fittings (solid lines on the dots) and the results of the decompositions are also given. All the spectra are taken at a photoelectron emission angle (θ_e) of 0° (along the surface normal).

The energy separation between P_1 and P_2 (0.35 eV) reflects the charge transfer from the down- to the up-dimer atom for the asymmetric dimer formation. The corresponding core-level shifts for Si and Ge asymmetric dimers have been known to be in a similar energy range of 0.6–0.8 eV (Refs. 24 and 28) and 0.2–0.3 eV,[29] respectively. Within this interpretation P_1 and P_2 correspond to down- and up-dimer atoms, respectively, that is, the electron-poor (higher binding energy) and electron-rich (lower binding energy) environment.[28] Only very recently a rather clear evidence of such buckling is provided by an STM study.[14] That is, in Ref. 14, the dimers along a single Pb adsorbate chain are shown to be buckled in the same direction (''ferromagnetically'') but the buckling direction of neighboring chains is opposite (''antiferromagnetical''). Such a buckling leads to a local 2×4 periodicity, in contrast to the buckling configuration of Si and Ge dimers buckled antifferomagnetically even along the chains. The origin of this difference is not clear at present. Similar parallel dimer chains have also been observed during the very initial homoepitaxial growth of Si on Si(001), which are called ''dilute dimer chains.''[1–3,30] However, though there are quite a few theoretical and experimental studies on the Si parallel dimer chains, no explicit discussion of the possible dimer buckling can be found in the literature.

With increasing the Pb coverage from 0.60 to 0.75 ML, the spectra become slightly shaper and asymmetric. There is a long tail and a shoulder (see the vertical line in Fig. 3) in the lower kinetic energy side. The spectrum for 0.75 ML is decomposed into two components (denoted as P_3 and P_4) in asymmetric (Doniach-Sunjic) line shapes with a singularity parameter of 0.09. The asymmetry (the long low-energy tail) indicates a metallic response of the surface electrons. P_3 and P_4 components are slightly sharper than those below 0.60 ML with a Gaussian width of 0.38 eV. The ratio between P_3 and P_4 is roughly 1:3. At a coverage of 0.75 ML, LEED shows a very well ordered $c(8\times4)$ phase[31] and the available structural models of this phase are given in Figs. 1(c) (Ref. 13) and 1(e) (Ref. 11). These models were introduced to explain the characteristic STM images of the $c(8\times4)$ phase and are commonly composed of *buckled* Pb dimers. The nominal coverages of these models are 0.75 ML, in agreement with the present and previous LEED observations.[10,11,15] Another variation of the $c(8\times4)$ structure model introduced is shown in Fig. 1(d) where one-third of the Pb dimers of the model in Fig. 1(c) is replaced by Si dimers and hence the Pb coverage is 0.5 ML. We observe no trace of ×4 spots at around 0.5–0.6 ML, in contrast to this model, and further this model is not compatible with our Si $2p$ result discussed below. Then the major difference between the models of Figs. 1(c) and 1(e) are the orientation of the Pb dimers; orthogonal and parallel to the Si substrate dimers, respectively. Hence, in the model of Fig. 1(c) [or 1(d)], the Pb dimers have to be totally rearranged, i.e., rotated by 90°, when forming the $c(8\times4)$ phase from the 2×2 parallel dimer chain phase. A recent total energy calculation suggested that the model in Fig. 1(c) is energetically stable.[12] However the structure model in Fig. 1(d) and other possible structures have never been tested energetically. This obviously prevents a consistent comparison of the energetics of different models.

However, in any case, these models are apparently not compatible with the present Pb $5d$ core-level spectra, since all of these models are composed of buckled dimers leading to equally weighted double $5d$ components. That is, the Pb $5d$ core levels of the $c(8\times4)$ structures composed of buckled dimers is expected to be qualitatively the same as that of 2×2. Obviously this is not the case in the present experimental result. It is clearly suggested that the present structure models of the $c(8\times4)$ phase should be reconsidered. This point will be mentioned again after the analyses of the Si $2p$ core levels below.

In clear contrast to the 2×2 and $c(8\times4)$ phases, the 2×1 phase at 1.0 ML exhibits a sharp single component with a Gaussian width of 0.33 eV, indicating only one adsorption site for Pb. This spectrum is dressed with an apparent metallic tail at the low-energy side with a rather large asymmetry parameter of 0.14. It suggests that the 2×1-Pb surface has a metallic character. This corroborates the results of the previous angle-resolved photoemission study for the valence bands, which indicated the metallization of the Pb/Si(001) surface.[23] In that study, the photoemission intensity at Fermi level appears from a Pb coverage of ∼0.7 ML and it increases along with the increase of the Pb coverage, correlated to the formation of the metallic 2×1 phase.

At present there are two available structure models for the 2×1-Pb surface, as shown in Figs. 1(f) and 1(g). In one model [Fig. 1(f)], Pb adsorbates have two different kinds of adsorption sites, one on top of Si dimer atoms and the other in the hollow sites between Si dimers.[32] This model definitely disagrees with the observed Pb $5d$ spectra, which indicate only single adsorption site. Furthermore, the nominal coverage of this model is 1.5 ML, while most of the LEED studies observed clear a 2×1 pattern from 1.0 ML including the present observation.[10,11,15] Within the alternative model [Fig. 1(g)], Pb atoms form symmetric parallel dimers.[11] This 2×1 structure is compatible with the Pb $5d$ core level. Note that this structure is different from the case of the Ge or Si monolayer structure on Si(001), where the surface phase is 1×2 with asymmetrically buckled orthogonal (to the substrate dimer orientation) dimers.[2–5] The 2×1 orientation of the phase at 1 ML Pb was previously confirmed unambiguously by observing the LEED patterns for the growth on a single-domain Si(001)2×1 surface.[23] The 2×1-Pb structure is not in the proper crystallographic stacking within the diamond structure. Within the symmetric parallel dimer model of 2×1, the surface is thought to be metallic due to the two half-filled dangling bond electrons on each Pb dimer in consistency with the core-level and the valence-band[23] photoemission results. An analogous metallic situation can be found for the case of the symmetric dimer model of the Si(001)2×1 surface.[33] However, it is not clear why the Pb dimers are all *symmetrized* within the 2×1 unit cell. A further theoretical study is highly requested to clarify the atomic and electronic structures of the $c(8\times4)$ and 2×1 phases.

Figure 4 shows a series of Si $2p$ core-level spectra taken at a photon energy of 130 eV with an emission angle of 60° to enhance the surface sensitivity. The spectrum at the bottom, which was obtained from the clean Si(001)2×1 surface, exhibits a prominent peak (denoted as S_u) at the low binding-energy side. The S_u component corresponds to the buckled-up atoms of the asymmetric Si dimers.[24,28] As the Pb

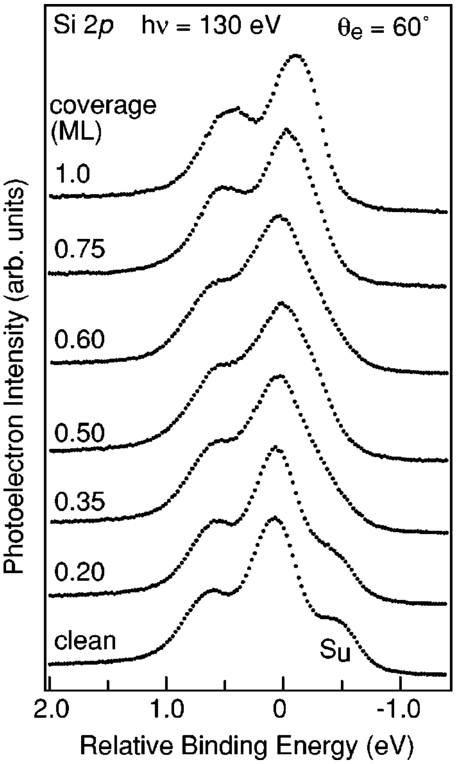

FIG. 4. A series of Si $2p$ core-level spectra for the same Pb/Si(001) surfaces as in Figs. 2 and 3 taken with a photon energy ($h\nu$) of 130 eV at an emission angle (θ_e) of 60°.

atoms are deposited, S_u gradually disappears and almost no intensity of it is found beyond 0.5 ML. This behavior is consistent to the parallel dimer structure models of the 2×2 and 2×1 surfaces, where all Si surface atoms are bonded to Pb adsorbates without no bare Si dimers left. As mentioned above this result rules out any structure models with Si buckled dimers within the topmost layer, like that in Fig. 1(d), for the coverage larger than 0.5 ML. Other than the disappearance of S_u, the changes of the spectral shape at different coverages are rather subtle, requesting careful curve-fitting analyses. We took more than five different high-resolution spectra for each phase at different photon energies and at different emission angles and found a unique fitting solution over such a set of spectra for a given phase. This kind of procedure minimizes possible arbitrariness of the curve-fitting analyses.[21,24] The results of the curve fittings of the spectra for the 2×2, $c(8\times4)$, and 2×1-Pb surfaces are shown in Fig. 5. The spectra at normal ($\theta_e=0°$) and grazing ($\theta_e=60°$) emission angles are compared to show the surface sensitivity of each component.

As seen in Fig. 5(a), Si $2p$ for the 2×2 surface exhibits two major components other than the bulk component *B*, denoted as S_1 and *D*. The appearance of S_1 can barely be seen in the raw spectra at $\theta_e=60°$ in Fig. 5(a) in which a weak but discernible shoulder appears (see the arrow in the figure). The S_1 component shows obvious surface sensitivity and it is straightforwardly assigned to the Si atoms in the topmost Si layer bonded to Pb adsorbates. Pb adsorbates make Si dimers symmetric by saturating Si dangling bonds, which then appears as S_1 instead of S_u in Si $2p$ spectra. The intensity of S_1 is roughly twice as large as that of S_u on the clean surface. This is consistent to the 2×2 structure model with a full monolayer of Si bonded to Pb: S_u represents only the up-dimer atoms of 0.5 ML. The binding energy shift of S_1 from the bulk component *B*, the so-called surface core-level shift (SCLS), is determined as -0.22 eV (see Table I). The other major component *D* is thought to be due to the second Si layer since its SCLS and intensity are very similar

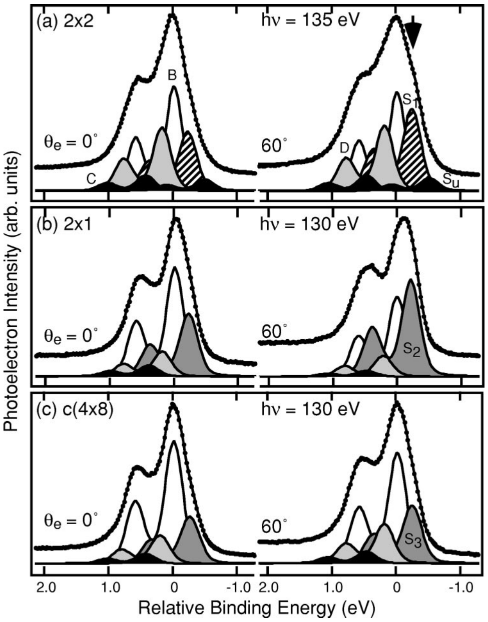

FIG. 5. Decompositions by curve-fitting analyses of the Si $2p$ core-level spectra for (a) Si(001)2×2-Pb at 0.5 ML, (b) 2×1-Pb at 1.0 ML, and (c) $c(8\times4)$-Pb at 0.75 ML. The spectra are taken with photon energies of (a) 135 and (b, c) 130 eV at emission angles (θ_e) of 0° and 60°. Experimental data (dots) are superimposed with the results of the least-square curve fittings (solid lines on the dots) and the results of the decompositions are given with different hatchings.

TABLE I. The major curve-fitting parameters using spin-orbit doublets in Voigt function form optimized for the spectra shown in Fig. 5. The surface core-level shift (SCLS), binding energy shift from the bulk component *B*, and the Gaussian width of each decomposed component are given.

Structure	Component	SCLS (eV)	Width (eV)
2×2-Pb	*B*	0	0.24
	S_1	-0.22	0.28
	D	0.19	0.28
	C	0.45	0.28
$c(4\times8)$-Pb	*B*	0	0.28
	S_3	-0.23	0.30
	D	0.21	0.30
	C	0.49	0.30
2×1-Pb	*B*	0	0.26
	S_2	-0.22	0.28
	D	0.25	0.28
	C	0.55	0.30

to the second layer component of the clean Si(001)2×1 surface.[21,24] This close similarity further suggests that the second Si layer is only marginally altered by Pb adsorption as expected from the preserved Si dimerization in the 2×2 structure model and from the covalent bonding between Pb and Si.[23] In further support of the parallel dimer model of the 2×2 phase and the present assignment of the Si 2*p* components, the Si 2*p* core levels of the In-induced 2×2 parallel dimer structure on Si(001) are essentially identical to those of 2×2-Pb. The SCLS of the corresponding S_1 component is −0.19 eV for the 2×2-In structure. The origin of a minor intensity component *C*, observed at high-binding-energy side for all three phases (Fig. 5), is not clear but is thought to be due to defects or a contamination on the surface.

The Si 2*p* core levels of the 2×1 surface at 1.0 ML [Fig. 5(b)] are decomposed into only two major components: *B* and a surface-sensitive component S_2. Although the raw spectra themselves are rather featureless, the existence of S_2 is obvious from the noticeable shift of the apparent peak maximum to a lower binding energy from normal to grazing angles. The S_2 component is naturally attributed to one full monolayer of Si atoms bonded to Pb adsorbates. This is consistent with the 2×1 parallel dimer model. The SCLS of S_2 is slightly larger (−0.23 eV) than that of S_1, which would reflect the chemical and structural changes of the topmost Si layer, that is, the breaking of Si dimer bonding and the increase of Pb-Si coordination number (Fig. 1). The absence of a large second Si layer component *D* is also qualitatively understood from such changes of the first Si layer; the release of Si dimerization leads to a more bulklike environment for the second Si layer.

For the case of the *c*(8×4) phase, the spectral shape and its decomposition are qualitatively in the middle of the 2×2 and 2×1 phase. The surface-sensitive component S_3 with a SCLS of −0.23 eV can consistently be assigned to the Si atoms bonded to Pb in the first Si layer. Then its intensity suggests that the number of Si atoms bonded to Pb does not amount to 1.0 ML. However, any further insight into the *c*(8×4) structure could not easily be provided from the present Si 2*p* analyses. We finally comment about the possible structure model of the *c*(8×4) phase. As mentioned above, the present structure models of this phase [Figs. 1(c), 1(d), and 1(e)] based on the asymmetric dimers cannot be reconciled with the Pb 5*d* spectral shape. If the parallel dimer 2×1 model is correct, then further doubts are cast onto the *c*(8×4) model of orthogonal dimers such as those in Figs. 1(c) and 1(d). This is because such structure models require the 90° rotation of all surface Pb dimers for the 2×2-*c*(8×4) phase transformation and again back-rotation for the *c*(8×4)-2×1 transformation, which obviously accompany a large energy cost. Then, the correct model should be composed of two different Pb sites with different populations, as indicated by the Pb 5*d* data and the major Pb site could be close to the parallel Pb dimers. As far as we have tried, any simple structure model with such constraints and with a Pb coverage of 0.6–0.8 ML was not successful in explaining the characteristic STM images. A more elaborate theoretical study is needed to solve this issue.

IV. CONCLUSION

High-resolution core-level photoemission spectroscopy using synchrotron radiation and LEED have been applied to study the surface reconstructions induced by Pb adsorption on the Si(001) surface at room temperature. The present LEED study observed a serious of LEED patterns of 2×2, *c*(8×4), and 2×1 for the Pb coverages of 0.5, 0.75, and 1.0 ML, respectively, in consistency with previous reports.[10,11,15] In addition ×2 streaks and a diffuse 2×3 pattern are observed for 0.2–0.3 and 0.35 ML, respectively. These newly found features in LEED are similar to the initial growth of Al, Ga, and In on Si(001),[19] indicating a certain interchain interaction of 1D Pb dimer chains. Pb 5*d* spectra below 0.6 ML are essentially the same with two components of an equal intensity. This clearly evidences the buckling of Pb dimers formed on the surface in consistent with recent STM (Ref. 14) and theoretical[12] results. The Si 2*p* component for the topmost Si layer bonded with Pb dimers is identified. These results are fully consistent with the asymmetric parallel dimer model of the 2×2 phase.[12,14] However, for the case of the *c*(8×4) phase at 0.75 ML, two Pb 5*d* components appear with an intensity ratio of ∼1:3. This is in contradiction to the currently available structure models composed of buckled Pb dimers as in the 2×2 phase. At 1.0 ML a well-ordered 2×1 phase is observed, which exhibits a sharp Pb 5*d* level with single component. This result favors the 2×1 model with symmetric and parallel Pb dimers. The Si 2*p* component for the topmost Si layer is also resolved. The Si 2*p* decomposition further suggests the release of the Si dimerization underneath the Pb layer in consistency with the 2×1 parallel dimer model. The Pb 5*d* line-shape analyses also show long inelastic tails at 0.75–1.0 ML, corroborating the metallization of the surface when forming the 2×1 phase as reported by a recent valence-band photoemission study.[23]

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