

INTRA-ATOMIC CHARGE RE-ORGANIZATION AT THE Pb-Si INTERFACE: BONDING MECHANISM AT LOW COVERAGE

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Many studies of adsorption of group IV elements on the group IV substrates have been reported in the past decade, but many questions are still open. The most curious and intriguing system is Pb on a Si(111) surface, which shows phase transitions and phase co-existence, in-commensurate structures and similar effects that depend extremely strongly on Pb coverage[1]. If the structure of $(\sqrt{3} \times \sqrt{3})R30^\circ$ (denoted as $\sqrt{3}$ hereafter) with 1/3 monolayer (ML) of Pb coverage has a unit cell that contains one metal atom located at the T_4 site of the Si(111) surface, it is conventionally called β phase (denoted as). When cooled, the layer transforms to the incomplete (3×3) structure, with three metal atoms per unit cell in two different chemical states[2]. The two states were identified by core level photoemission experiments for both the $\sqrt{3}$ and (3×3) structures. A widely accepted model is based on different vertical heights of metal atoms above the surface resulting in charge redistribution between these distinct states and the presence of surface soft phonons. On reducing the coverage to 1/6ML – to the γ - phase (hereafter), an alloy with the same symmetry – the $\sqrt{3}$ – is found containing 1/6 ML of Si and 1/6 ML of Pb atoms in a single chemical state. The Si and Pb atoms forming the chemically disordered phase occupy the same T_4 position. The γ phase is found to be more stable than the β experimentally. The relation between the single chemical state in the phase and two states in the β phase is crucial for a full understanding of the charge transfer effect in the system and the bonding character in particular phases. The model based on different vertical heights of Pb atoms at T_4 sites was successfully introduced with ab initio calculations for the Pb/Si(111) system [3]. The height of the Pb atoms above the T_4 site calculated by Density Functional Theory (DFT) pseudopotential method depends strongly on the valence band electronic configuration of an applied Pb pseudopotential. In particular, the pseudopotential

including $6s2\ 6p2$ states in the valence band produces the β with atoms at constant height above the substrate. Involving the shallow $5d$ outer core levels in the valence states of the pseudopotential produces an arrangement of one Pb atom up and two down in the (3×3) unit cell, which is the ratio found with photoemission[4]. This effect underlines the importance of the $5d$ electrons in the charge transfer and screening. DFT calculations of the charge redistribution in real space are needed to get an insight into the formation of the $\sqrt{3}$ phase on the Si(111) surface and to understand the bonding of Pb with an isoelectronic substrate. This point is extremely important as two competing models, soft phonons and charge density waves, are based on the redistribution of charge between the Pb and Si atoms. The one up and two down arrangement of Pb atoms is understood as a dynamic exchange of up and down positions keeping the ratio between them constant. The process is too fast for the time resolution of the STM (Scanning Tunneling Microscope), which gives an image of atomic position averaged over micro to milliseconds. The experimental characterization of an adsorption site on a fast time scale we did using photoemission and photoelectron diffraction (PhD). The spectrum reflects the local arrangement of neighbouring atoms with a time resolution of femtoseconds. The fit of experimental PhD patterns we did with the Van Hove code. In this contribution, we present experimental and theoretical studies of the 1/3 ML and the 1/6 ML Pb/Si(111) phases by means of energy scanned photoelectron diffraction and DFT calculations. We found that the "one up and two down" model is a good description of the β phase. DFT calculations show a localized rearrangement of charge at particular Si atoms in the second layer participating in the Pb-Si bonding.

The measurements were carried out at the Czech Materials Science Beamline, Elettra synchrotron light

source, Trieste, Italy. The desired coverage of Pb was achieved by evaporating several monolayers (ML) of Pb at room temperature onto the clean Si(111)–7×7 surface, and then progressively desorbing the Pb by annealing at constant temperature for fixed time intervals [4]. 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 here has an angular acceptance of half cone angle up to 8°. The photoemission spectra were used to monitor the quality of the β and γ phases and ensure that they had stoichiometric coverage of 1/3 and 1/6 ML. The Pb 5*d* lines were sharpest at coverage of 1/6 ML or less, while a clear two-component doublet was observed for 1/3 ML. The LEED (Low Energy Electron Diffraction) pattern was checked and found to give the best (√3×√3) patterns for these coverage. We measured photoelectron diffraction spectra of the Pb 5*d* core levels for the β and γ phases. The variation of peak intensities was measured as a function of photon energy and the data were acquired as Energy Distribution Curves (EDC) in three basic geometries (polar angle): normal emission (NE), off-normal emission (28°) and grazing emission (55°) at a fixed angle of 60° between the analyser and the incident beam. The azimuthal angle was kept constant and for off-normal conditions was approximately along the Γ – K direction of the Si(111)–(1×1) surface Brillouin zone. The angular resolution of the analyser was kept at ±4°. The photon energy was changed by steps of 1 eV in the interval 50–150 eV producing Pb 5*d* photoelectrons with kinetic energy in the range 30 to 130 eV.

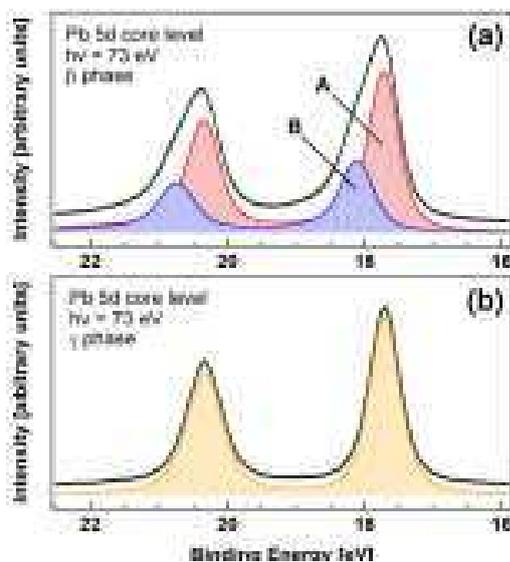


Figure 1. Core level spectra for the Pb/Si(111) β and γ phases measured at NE geometry. One of the two states in the β phase is identical with the single state of the γ phase.

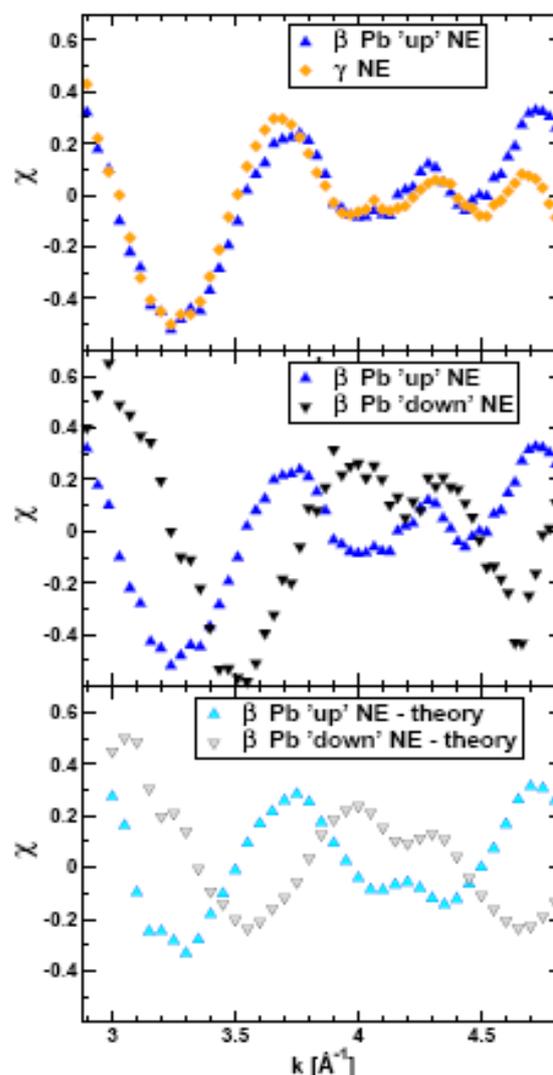


Figure 2. 5*d* core level diffraction in the NE geometry of the Pb atoms on the γ phase and up and down Pb atoms on the β phase with theoretical simulation.

We used the pseudopotential local orbital Fireball code [5] based on density functional theory (DFT). This code was developed with the aim of providing a very favourable accuracy/efficiency balance if an atomic-like basis set is chosen appropriately. The valence wavefunctions are expanded in the Fireball orbitals, a set of strictly localized pseudoatomic orbitals (they are exactly zero for distances larger than the cut-off radius (RC). In our case, Si valence states were represented by a basis set including *s*, *p* and *d* Fireball orbitals with the following parameters: RC (Si, *s*-orbital) = 4.8 Å, RC (Si, *p*-orbital) = 5.4 Å. and RC (Si, *d*-orbitals) = 5.2 Å. This basis set yields a very good description of the bulk properties of Si, as well as the Si(111)–(7×7) reconstruction; for the bulk diamond structure we obtained a lattice parameter *a* = 5.46 Å and a bulk modulus *B* = 105 GPa (experiment: *a* = 5.40 Å, *B* = 100 GPa). For Pb, we used a pseudopotential involving the 6*s*2 6*p*2 5*d*10 states of Pb in the valence band electronic configuration. We applied this particular configuration to optimize electronic structure according to the local

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atomic arrangement. The Fireball orbitals of the Pb atom had the following parameters: RC (Pb, *s*-orbital) = 5.4 Å, RC (Pb, *p*-orbital) = 5.9 Å and RC (Pb, *d*-orbitals) = 5.2 Å. In our calculations, we have used a supercell approach to model the Pb/Si(111) – $\sqrt{3}$ surface. First we have considered a (3×3) periodic slab that includes 3 Pb adatoms, 6 Si layers underneath and hydrogen atoms saturating the bonds of the deeper Si layer. The last two layers of the slab, the deeper Si and passivated H layer, were kept fixed during the relaxation process. The supercell contained 66 atoms, in total.

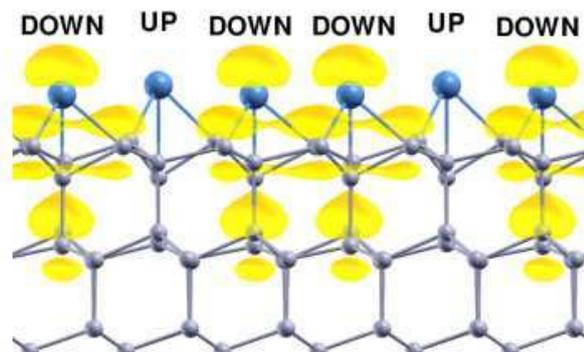


Figure 3. Surfaces of constant charge density 0.01 eV integrated over the range -0.1..0.1 eV around EF are projected onto the ball-and-stick model of the calculated 3×3 structure with the up and down Pb atoms. The surfaces are transparent yellow, Pb atoms are blue and Si grey. The absence of charge density on the Pb up and on the underlying Si atoms is apparent.

To understand better the electronic structure of the system, we plot a surface of constant real-space density of states near EF in Fig. 3. The figure displays the different charge distribution on the β surface with the up and down Pb atoms with particular triangular bipyramids. For the Pb down position, a considerable amount of the charge is located between a Pb atom and a SiT₄ one near the Fermi level. This feature is missing for the SiT₄ atom beneath the up Pb atom indicating a weak interaction between these two atoms. The dangling bonds of the up Pb adatoms are pushed deeper into the valence band and the triangular bipyramid shows a

semiconducting character. To summarize, the movement of Pb atoms up or down causes the redistribution of the charge within a covalent bond, not between the dangling bonds, contrary to the case of the Sn p3 structure. The redistribution is limited to the triangular bipyramids and it lacks the extended character of charge density waves. The proximity of the Pb-SiT₄ distance to the ideal Si-Pb bond length gives rise to a special type of binding in the bipyramid.

We found that the Pb/Si(111)– β is stabilized with the dynamic, intra-atomic charge redistribution as an interplay between the band structure and elastic deformation energy. It is the result of the interaction between the adsorbed unsaturated Pb atom and saturated underlying Si atom in the T₄ position. The extra bonding between them is localised in the triangular bipyramid. The dynamics occurs by the flipping of the Pb atoms between the up position, characteristic in the γ phase, and the down position. The effect causes the switching of a triangular bipyramid between metallic and semiconductor states in the agreement with experimental data. The combined study of PhD and ab initio DFT calculations contributes significantly to the understanding of the bonding of the two iso-electronic elements Si and Pb. Influence of defects on the stability of the β phase has been analysed using DFT calculations. The direct correlation between the local electronic state and vertical position of Pb adatoms has been identified.

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