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Electronic properties of experimentally observed Pb/Ru(0 0 0 1) adsorbate structures: A DFT study

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ABSTRACT

First-principles DFT calculations were carried out to investigate surface electronic properties of the experimentally established ((1/2)ML)-$c(4\times 2)$ and ((4/7)ML)-($\sqrt{7}\times\sqrt{7}$) phases of the Pb/Ru(0 0 0 1) adsorption system. Despite adatom arrangements of a different geometry for these two Pb phases, similar changes in the substrate electronic structure are induced by each overlayer formation, due to a relatively small difference in Pb film density. Bonding of the Pb adlayer to the Ru substrate is shown to involve a strong hybridization of Pb *p* states with Ru *d* states, which affects the energy distributions of the surface density of states, including surface *d*-band broadening (by almost 0.2 eV) and its shift towards lower energies (by 0.1 eV), and causes substantial spatial redistribution of electronic charge within the surface region of Pb/Ru(0 0 0 1), leading to alternating areas of some electron excess on the outside of Pb adatoms, pronounced electron depletion within the Pb overlayer and dominant electron accumulation between the adsorbate and the topmost Ru plane. The total charge transfer of $-0.13\,|e|$ to $-0.17\,|e|$ is found from Pb adatoms to the substrate, so they become positively charged, consistent with the predicted work-function decrease (by about 0.7 eV) upon Pb deposition. A generally covalent bonding of Pb to Ru with relatively little ionic character is concluded.

1. Introduction

Monolayer bimetallic surfaces, such as surface alloys or metal-on-metal adsorption systems, often exhibit unique physical and chemical properties as compared to unmodified bare surfaces of individual components, which makes them interesting for both basic surface-science research and prospective applications (see, e.g., Refs. [1–3] and references therein). The relevant issues in studying such systems include adlayer adhesion to the substrate, which depends on energetics of the adsorption process, and the morphology of the thin film, which may additionally be kinetically driven, but first of all the mutual interactions between the host and the additive, which determine the observed structural and electronic properties of a bimetallic surface. With the help of model adsorption systems, these properties can be investigated in a systematic and controlled manner.

Lead is one of the adsorbates studied in this respect for practical applications as well as fundamental aspects. Indeed, on some substrates, e.g., for Pb/Si(1 1 1) [4], Pb/Cu(1 1 1) [5], Pb/Ni(1 1 1) [6], or Pb/Mo(1 1 0) [7], the growth of multilayer Pb films is driven by quantum size effects, whereas the first wetting Pb layer can exhibit peculiar super-diffusive collective motion [4,8]. Adsorbed on the open Ru(1 0 $\bar{1}$ 0) surface, Pb forms a super-dense phase of unusual properties, including a quenched reactivity towards oxidation [9]. On the other hand, Pb is commonly used as a surfactant for a controlled growth of other elements [10] or as a means of altering the catalytic reactivity of the substrate, with both poisoning and promoting effects being recognized [11,12].

In the present paper, we address the Pb/Ru(0 0 0 1) adsorption system, which remains relatively unexplored despite the fact that the close-packed ruthenium surface is an important substrate in catalysis [13]. While the Stranski–Krastanov mechanism of growth of Pb on the Ru(0 0 0 1) surface was unambiguously established by Liu et al. already a decade ago [14], no structural details of the first wetting layer were reported. Only very recently, Yuhara et al. using LEED and STM [15], and Jurczyszyn et al. using LEED and AES [16], revealed the formation of long-range ordered submonolayer adsorbate structures of the $c(4\times 2)$ and ($\sqrt{7}\times\sqrt{7}$) geometry. The former, consisting of Pb islands with adlayer density of 1 Pb adatom per 2 Ru surface atoms, was observed for a wide range of low Pb depositions up to (1/2) ML. The latter, identified at the coverage of (4/7) ML, corresponds to the densest Pb packing within the first adlayer. Based on total-energy calculations within the framework of density functional theory (DFT), the optimal atomic arrangements of these two distinct Pb/Ru(0 0 0 1) phases were predicted and their structural properties were characterized in detail in Ref. [16]. Here, using the same DFT approach, we investigate the electronic properties of

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the experimentally recognized ((1/2)ML)-$c(4\times 2)$ and ((4/7)ML)-$(\sqrt{7}\times\sqrt{7})$ Pb/Ru(0 0 0 1) adsorbate structures.

Liu et al. [14], who studied the interactions of ultrathin Pb films with the Ru(0 0 0 1) substrate by means of XPS, pointed out several mechanisms, often of an opposite effect, as a possible origin of the observed Pb core-level binding-energy shifts with increasing Pb coverage, including hybridization of adatom orbitals, density-of-states (DOS) redistribution within the substrate conduction band, and the charge transfer between the different metal atoms. Since the related theoretical analysis is missing, in this work we elaborate on these issues by simulating the effects of Pb adsorption on the electronic characteristics of the Ru(0 0 0 1) surface within DFT. The DFT modeling enables us, in particular, to examine modification of the surface electronic DOS upon Pb adsorption and follow the corresponding space-charge redistribution within the system for all Pb/Ru(0 0 0 1) phases established experimentally at submonolayer Pb coverages [15,16]. We believe that these results shed more light on the relative role of the adsorbate–adsorbate and the adsorbate–substrate interactions in the formation and the properties of ultrathin Pb overlayers on Ru(0 0 0 1).

2. Computational method

First-principles DFT calculations were carried out using the Vienna ab initio simulation package (VASP) [17]. The projector-augmented wave (PAW) method [18] and the gradient-corrected Perdew–Burke–Ernzerhof (PBE-GGA) exchange-correlation functional [19] were applied. All computations were performed in a non-collinear fashion taking into account spin–orbit interactions, as required for a reliable description of systems containing the relatively heavy Pb atoms. On the other hand, spin-polarization corrections occurred negligible (as expected for nonmagnetic elements), and therefore, were not accounted for.

Following Ref. [16], the Ru(0 0 0 1) substrate was modeled by a five-layer slab with three bottom layers frozen in bulk positions and two top layers allowed to relax in the course of structural optimization. As it was checked, further increase of the slab thickness and/or the number of relaxed layers virtually did not alter the main structural and electronic characteristics of the considered surface, in particular the topmost layer contraction of 3.6% and the surface free energy of 162 meV/Å^2. Moreover, the predicted Ru(0 0 0 1) surface relaxation agreed with earlier DFT results [20] as well as the recently reported single-terrace LEED data [21]. Adsorption of Pb was simulated on the fully relaxed slab surface only. Appropriate dipole corrections were taken into account to compensate the slab asymmetry. The vacuum region within the supercell was about 20 Å thick to ensure decoupling of the consecutive slabs. Different surface unit cells were considered to reproduce the experimentally observed lateral periodicity of the Pb/Ru(0 0 0 1) adsorption system.

A cutoff energy was set to 350 eV throughout the computations. The Monkhorst-Pack Γ-centered **k**-point grids ranging from $(5\times 5\times 1)$ to $(9\times 9\times 1)$ were applied for Brillouin zone sampling, according to the size of the surface unit cell. Electronic and structural relaxations were performed using the Davidson-block algorithm and the conjugate-gradient method, respectively, until the energies converged to less than 10^{-5} eV and the forces acting on unconstrained atoms converged to less than 0.01 eV/Å. To accelerate electronic relaxations, the Methfessel–Paxton method of Fermi-level broadening was applied with the smearing width $\sigma = 0.1$ eV, but total energies extrapolated to the $\sigma \to 0$ limit were considered.

The calculated lattice parameters of hcp Ru crystal $a_{\rm Ru} = 2.728$ Å and $c_{\rm Ru}/a_{\rm Ru} = 1.575$, obtained from optimization of its bulk unit cell, are close to experimental values $a_{\rm Ru,exp} = 2.71$ Å and $c_{\rm Ru,exp}/a_{\rm Ru,exp} = 1.58$ [22]. For the fcc Pb crystal, the computed lattice constant $a_{\rm Pb} = 5.05$ Å is also slightly overestimated with respect to the experimentally established $a_{\rm Pb,exp} = 4.95$ Å, but the cohesive energy $E_{\rm coh,Pb} = 2.01$ eV almost coincides with the measured heat of Pb sublimation of 2.03 eV/atom [22].

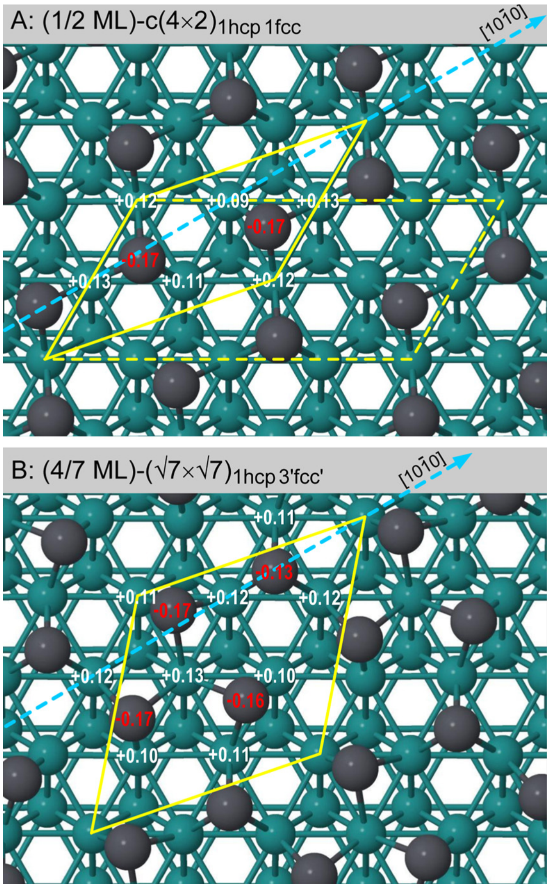

Fig. 1. Schematic ball-and-stick models (top view) of the optimal Pb/Ru(0 0 0 1) adlayer configurations predicted by DFT for experimentally observed adsorbate phases: (a) $c(4\times 2)_{\rm 1hcp1fcc}$ structure at $\Theta_{\rm Pb} = (1/2)$ ML, (b) $(\sqrt{7}\times\sqrt{7})_{\rm 1hcp3'fcc'}$ structure at $\Theta_{\rm Pb} = (4/7)$ ML. Dark-gray and green spheres represent Pb and Ru atoms, respectively. Red and white numbers describe the change of the effective number of valence electrons at particular atoms, $\Delta N_{\rm el}$, calculated with respect to isolated ones using the Bader scheme, with negative (positive) values indicating depletion (excess) of electrons, i.e., positive (negative) charging. The corresponding primitive (conventional) surface unit cells are depicted by solid (dashed) yellow lines. Dashed blue lines indicate [1 0 $\bar{1}$ 0] directions along which differential electron density is plotted in Figs. 2 and 3, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

3. Results and discussion

In this work, we focus on electronic properties of the Pb/Ru(0 0 0 1) adsorbate structures recognized experimentally at submonolayer Pb coverages, namely, the ((1/2)ML)-$c(4\times 2)$ and ((4/7)ML)-$(\sqrt{7}\times\sqrt{7})$ phases [15,16]. The optimal (i.e., energetically most favorable) adatom arrangements corresponding to these two phases were already postulated, based on the same kind of DFT simulations, and characterized in detail in Ref. [16]. Recollecting briefly their structural properties, the ((1/2)ML)-$c(4\times 2)$ phase contains two Pb adatoms in the primitive surface unit cell occupying the slightly distorted hcp and fcc sites in the 1:1 proportion (cf. Fig. 1(a)), whereas the ((4/7)ML)-$(\sqrt{7}\times\sqrt{7})$ structure contains four Pb adatoms in the primitive surface unit cell occupying one virtually undistorted hcp site and three strongly distorted fcc-like positions, referred to as ‘fcc’ sites (cf. Fig. 1(b)). As a matter of fact, another