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Pb chain-like structures on the clean Si(001) surface — A DFT study

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ABSTRACT

The adsorption of lead (Pb) atoms on the clean Si(001)c(4×2) reconstructed surface as a function of the adatom coverage is investigated using density functional theory. It is shown that the growth of Pb adatom chains from the most stable monomer configuration, the end-dimer-bridge configuration, proceeds via the formation of inter- and intra-row ad-dimers, and ad-trimers. The calculated energetics of long Pb chains show that the most thermodynamically stable chains are composed exclusively of inter-row dimers, and that monomer termination of these chains is favoured over termination by a dimer.

1. Introduction

The formation of atomic chain-like structures by atoms of groups III and IV diffusing on the clean Si(001) surface has been investigated theoretically and experimentally for more than a decade [1–15]. These studies have shown that the chains formed on Si(001) at room temperature consist of pairs of adatoms (dimers) that are aligned along a line perpendicular to the Si-Si dimer rows of the reconstructed Si(001)2×1 surface. It has also been noticed that while the ad-dimers formed from the group III atoms such In, Al or Ga are symmetric [1,3,5,7,8], chains of Pb atoms (group IV) are composed of asymmetric Pb dimers; ie. the Pb adatoms forming the dimers have distinctly different vertical positions [9,11,13,14]. This difference may affect not only the efficiency and energetics of the chain growth process, but is also expected to influence the electronic (transport) characteristics of the formed chains. A better understanding of all the effects involved in 1D atomic chain formation is crucial for controlling the assembly of such structures, and tailoring their properties for various specific applications in Si-based nanocircuit technology.

Early studies of Pb on the Si(001)2×1 surface dealt with the energetics of various geometries of isolated Pb adatoms and dimers, and the corresponding energies of infinite chain structures [9,13,14]. However the energetics associated with the formation of long Pb-chains on a Si(001) substrate, and the stability of the different atomic configurations that appear during growth, have not been considered. Also, the electronic properties of the initial Pb chain configurations, which are important for understanding the mechanism underlying the growth of these chains, have not been studied. In this paper we consider, based on density functional theory (DFT) calculations, the structural, electronic and energetic characteristics of the different pathways associated with the one dimensional aggregation of Pb adatoms diffusing on Si(001). We also present the relative stability of the formed chains as a function of the Pb chemical potential (adatom concentration). Guided by the available experimental data, we have limited our study to the growth of one dimensional Pb chains along the $[01\bar{1}]$ direction; i.e. in a direction perpendicular to the silicon dimer rows. We show that for all chains of a given length, those that consist of inter-row Pb–Pb ad-dimers are the most thermodynamically stable configurations, irrespective of the growth process. We have also found that termination of these chains by a Pb monomer is always more stable than termination by a Pb ad-dimer.

2. Method

The data presented in this paper were generated by performing DFT total energy and electronic structure calculations using the Fireball code [16,17]. Local-orbital pseudo-atomic basis sets [18] were used in the calculations with the atomic cores described by pseudopotentials, and the exchange-correlation contributions by the local-density-approximation (LDA) functional of Ceperley and Alder [19].

The Si(001) substrate was modelled using the calculated bulk lattice constant of 5.46 Å, a six layer slab with the dangling bonds at the bottom of the slab saturated by hydrogen atoms, and a (8×6) surface unit cell. This allowed us to analyse the formation of chain-like structures with up to seven Pb adatoms. In the total energy

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calculations, the Pb adatoms and five topmost atomic layers of the slab were allowed to relax, while the positions of the rest of the substrate atoms were frozen in their bulk-like configuration. Relaxation of the atomic positions has been carried out using a combination of conjugate gradient and dynamical quenching algorithms. Electronic structure calculations were performed for all of the predicted thermodynamically stable Pb/Si(001) configurations.

The relative energetics of the various Pb chain structures formed on Si(001) have been analysed using the method of ab initio atomistic thermodynamics [20,21], where the availability of the Pb adatoms from the environment in thermal equilibrium is represented by the Pb chemical potential. For a given chemical potential of the Pb adatoms, the thermodynamically preferred surface is the one with the lowest surface free energy calculated from

$$\gamma = \frac{1}{A}\left[E_{Pb/Slab} - E_{Clean-Slab} - N_{Pb}\mu_{Pb}\right]$$

In this equation, γ is the surface free energy per unit surface area relative to the Pb-free c(4×2) reconstructed Si(001) surface, and N_{Pb} is the number of Pb adatoms with chemical potential μ_{Pb}. $E_{Clean\text{-}Slab}$ and $E_{Pb/Slab}$ are the DFT total energies of the clean slab, and the slab with the adsorbed Pb adatoms, respectively. Defining

$$\Delta\mu_{Pb} = \mu_{Pb} - E_{Pb}$$

where E_{Pb} is the energy of a free Pb atom, the above equation for the surface free energy can be rewritten in the form

$$\gamma = \frac{1}{A}\left[E_{Pb/Slab} - E_{Clean-Slab} - N_{Pb}\ E_{Pb} - N_{Pb}\ \Delta\mu_{Pb}\right]$$

This is the expression that we have employed in this work.

It should be noted that the above equations ignore the vibrational, entropy and pressure volume terms, all of which are expected to be small [21].

3. Results and discussion

3.1. Adsorption of a single Pb atom on Si(001)

As a first step, we considered the adsorption of a single Pb atom on the clean Si(001)c4×2 reconstructed surface. The four stable configurations that we found are shown schematically in Fig. 1.

In the configuration shown in Fig. 1(a), the Pb adatom bridges across the ends of two consecutive silicon dimers along a given dimer row ([011] direction) with a calculated adsorption energy of 3.72 eV. The two structures shown in Fig. 1(b) and (c) represent the inter-row bridging configurations in which the Pb adatom sits midway between either two adjacent Si-up atoms [Fig. 1(b)], or between two adjacent Si-down atoms [Fig. 1(c)], on neighbouring dimer rows. The calculated adsorption energies are 2.82 eV and 3.45 eV, respectively. Fig. 1(d) shows the adatom geometry where the Pb adatom is adsorbed at the intra-row site between two Si dimers of the same dimer row. The adsorption energy of this adatom was calculated to be 3.44 eV.

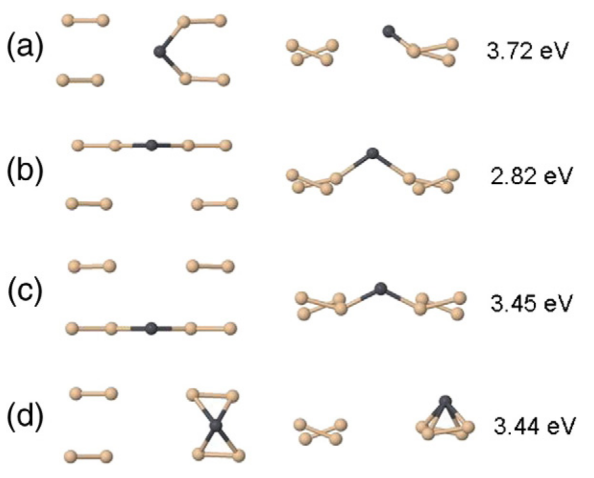

Fig. 1. Schematics of the stable monomer structures that result from the adsorption of a single Pb atom on the Si(001)c(4×2) surface. The corresponding values of the binding energies are also shown.

It follows from the calculated binding energy values that the end-dimer-bridge configuration of Fig. 1(a) is the most energetically favourable monomer configuration. This agrees with previous results [15]. The details regarding this configuration are given in Fig. 2. The two Pb–Si bond lengths are calculated to be essentially the same (2.71 Å and 2.72 Å) with the adatom located midway between the two Si atoms to which it is bonded. The buckled geometry of the two Si–Si dimers which interact directly with the Pb adatom is retained, although with the buckling angles reduced from 21.6° to 15.4° for the dimer bonding to the Pb via its up-Si, and from −21.6° to −10.5° for the down-Si bonding atom. While the dimer bond length associated with the up-Si bonding atom (2.40 Å) is close to that on the clean surface (2.39 Å), the dimer bond length of the down-Si bonding atom is elongated to 2.45 Å.

The local density-of-states (LDOS) projected on the Pb adatom, and the Si1 and Si2 substrate atoms, of the end-dimer-bridge structure, is shown in Fig. 3. Peak (a) in this figure, which is located just below the Fermi level ($E_F = 0$), has contributions from the p_x orbital of the Pb adatom and the p_z orbitals of the Si substrate atoms interacting with the adatom. The partial charge distribution associated with this state is presented in Fig. 4(a) and reveals an asymmetric charge distribution which results from the contribution from the silicon p_z orbital of the lower Si atom (Si_1 in Fig. 2) being considerably larger than that from the up-Si atom Si_2. This indicates that charge is redistributed from the Si-up atom to the Si-down atom, mediated by the Pb adatom. The second maximum in the LDOS of Fig. 3 [peak (b)] is located about 1.3 eV below the Fermi level. This peak originates from states associated with the p_y orbital of the Pb adatom and the p_z orbitals of the Si substrate atoms that interact directly with the Pb adatom. The partial charge distribution for this state is shown in Fig. 4(b).

3.2. Incorporation of a second Pb adatom into the most stable monomer configuration

Previous work by Chan et al. [15] has established that Pb atoms are very mobile on the Si(001) surface at room temperature with the maximum barrier between different adsorption sites being only 0.26 eV. In order to analyse the formation of Pb chain-like structures on the Si(001) substrate we assume that the second Pb adatom diffuses on the surface in the presence of the thermodynamically most stable structure — the end-dimer-bridge monomer configuration of

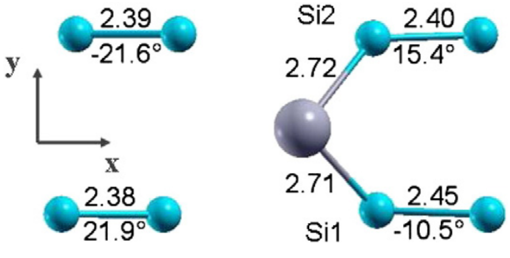

Fig. 2. Top view of the geometry of the end-dimer-bridge monomer structure of Fig. 1(a). The bond lengths are in Å. A positive buckling angle indicates that the atom on the left is higher than that on the right.