



# Interaction of a single acetophenone molecule with group III-IV elements mediated by Si(001)

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## ABSTRACT

A theoretical study of an influence of the acetophenone molecule adsorbed on the Si(001) on the local chemical reactivity of silicon surface is presented. The obtained results indicate that the interaction of the molecule with silicon substrate breaks the intra-dimer  $\pi$  bonds in four surface silicon dimers interacting directly with adsorbed molecule. This leads to the formation of two pairs of unpaired dangling bonds at two opposite sides of the molecule. It is demonstrated that these dangling bonds increase considerably the local chemical reactivity of the silicon substrate in the vicinity of the adsorbed molecule. Consequently, it is shown that such molecule bonded with Si(001) can stabilize the position of In and Pb adatoms diffusing on silicon substrate at two sides and initiate the one-dimensional aggregation of the metallic adatoms on the Si(001) substrate anchored at both sides of the adsorbed molecule. This type of aggregation leads to the growth of chain-like atomic structures in opposite directions, pinned to adsorbed molecule and oriented perpendicular to the rows of surface silicon dimers.

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## 1. Introduction

Traditionally, studies on semiconductor surfaces adsorbed by foreign species have been focused on either enhanced chemical reactivity of these substrates [1–3] or on their chemical passivation [4–7]. In the “bottom-up” approach, however, it is critical to construct on such substrates functional atomic/molecular systems in reactions that lead to their low-dimensional (0D or 1D) spatial organisation and functionality transfer. The intrinsic atomic and electronic anisotropies of the Si(001) surface provide an ideal platform for these type of reactions and their final tuning may open new avenues for this technologically important substrate.

On clean Si(001) two adjacent surface atoms pair into a Si-Si dimer and the formed dimers aggregate in parallel rows that extend over the entire surface. The charge within the dimer is not distributed evenly between the paired Si atoms because the dimers are tilted with the Si atom buckled up being electron-rich and the Si atom buckled down electron-deficient. The formation of the dimers is due to strong covalent  $\sigma$ -bonding between the Si dimer atoms while their buckling results from much weaker  $\pi$ -bond within the dimer (somewhat analogous to the C=C double bond in organic chemistry). On such dimerised and anisotropic surface, the freedom for a foreign atom or molecule to adsorb at a desirable location or along a preferred direction (by means of

selective or self-organised reactions) is hampered, however, by strong covalent bonds that are typically formed between the adsorbate and the Si substrate. Majority of the published studies have reported one-dimensional, self-assembled structures driven by the atomic anisotropy of hydrogenated Si(001) [8–11]. However, some other adsorption systems have also been identified to yield chemically driven, self-assembled structures guided by both the atomic and electronic anisotropy of bare Si(001) [12–22].

Self-assembly of chains from chemically bonded pyrazine ( $C_4H_4N_2$ ) molecules on bare Si(001) that run perpendicularly to the dimer rows was discussed by Shimomura et al. [19]. The formation of long, one-dimensional chains of physisorbed 1,5-dichloropentane molecules on clean Si(001) at room temperature was also reported [18]. Self-assembly into 1D atomic chains of inorganic elements such as In, Al, Ga, Ge, Pb, Sn, Bi [12–16], and rare earth element [17] were shown to spontaneously occur on clean Si(001) at room temperature. These atomic chains are formed in a perpendicular direction to the dimer rows but are randomly distributed on the substrate. A self-assembly of indium (In) and lead (Pb) chains, in the presence of a single organic molecule (benzonitrile) pre-adsorbed on bare Si(001), was demonstrated recently [23,24]. The reported results indicate that some organic systems can stabilize the position of metal ad-atom diffusing on the substrate surface and initiate one-dimensional aggregation of ad-atoms in the form of chain-like structures oriented perpendicularly to the Si dimer rows.

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**Table 1**

Upper panel: Bond-lengths in Å, and the buckling angles in degrees (in brackets) of the Si dimers which are in direct contact with the molecule adsorbed in Configurations C, A and B (a,b,c and d in Figs. 2–4). A positive buckling angle indicates that the atom on the left is higher than that one on the right.  
Lower panel: Inter-atomic distances in the systems shown in Figs. 1, 3 and 4 (acetophenone molecule in gas phase and adsorbed in configurations A, B). Symbols (numbers) are the same as in Figs. 1, 3 and 4..

		a	b	c	d	$E_{\text{ads}}$							
Upper panel	<i>acetophenone Config.C</i>	2.34 (21.56)	2.37 (−3.31)	2.39 (1.81)	2.44 (−9.92)	4.29							
	<i>acetophenone Config.A</i>	2.52 (−12.79)	2.38 (11.97)	2.47 (8.00)	2.39 (−10.81)	3.10							
	<i>acetophenone Config.B</i>	2.38 (11.97)	2.48 (−10.07)	2.41 (−11.41)	2.48 (9.87)	3.07							
Lower panel		1	2	3	4	5	6	7	8	9	10	11	12
	<i>acetophenone Config.A</i>	1.76	1.42	1.32	1.49	1.50	1.48	1.32	1.48	1.47	1.33	1.94	1.98
	<i>acetophenone Config.B</i>	1.73	1.47	1.32	1.49	1.33	1.48	1.48	1.31	1.48	1.50	1.96	1.97
	<i>acetophenone gas phase</i>	–	1.24	1.51	1.49	1.38	1.37	1.38	1.38	1.38	1.38	–	–

The revealed mechanism involves the local chemical modification of the Si(001) surface by the adsorbed molecule similar to that induced by C-defects on the Si(001) surface [1–3].

In this paper we investigate, using density functional theory, the reaction of an isolated acetophenone molecule with group III and IV elements mediated by the bare Si(001) surface. We show that from the three experimentally identified structures of the adsorbed molecule on Si(001) only the ones observed at low temperatures have a potential to trigger the self-assembly of group III and IV elements into atomic chains. Also, in contrast to the benzonitrile molecule, where the chains are anchored to the one side of the adsorbed molecule, the chains assembled in the vicinity of the adsorbed acetophenone molecule are expected to run across the Si dimer rows on both sides of the adsorbed molecule.

## 2. Methodology

Structural and electronic properties of the studied system were investigated using the density functional theory (DFT) as implemented in the Fireball code [25–27] using the local orbital pseudo-atomic basis set, the local density approximation (LDA) for exchange and correlation [28] and the norm-conserving pseudopotential [29].

The ground state Si(001)-c(2 × 4) reconstructed substrate was modelled within a large (8 × 6) surface unit cell using the asymmetric slab of six atomic layers constructed based on the calculated Si bulk lattice constant of 5.46 Å. The dangling bonds at the bottom of the slab were saturated by hydrogen atoms. In the total energy calculations, the coordinates of all the atoms within the four topmost atomic layers, and adsorbates, were allowed to relax; remaining atoms of the slab were frozen in their bulk-like positions. The relaxation of atomic position was carried out using the combination of conjugate gradient and dynamical quenching methods.

The adsorption energies (binding energies),  $E_A$ , of the adsorbates on Si(001) were calculated using the formula

$$E_A = -[E_{SM} - (E_S + E_M)]$$

where  $E_{SM}$  is the total energy of the surface with the adsorbate, and  $(E_S + E_M)$  is the energy of the surface not interacting with the adsorbate, both located within the same unit cell.

## 3. Results

### 3.1. An isolated acetophenone molecule on the Si(001)-c(4 × 2) surface

Recently published scanning tunneling microscopy (STM) experimental studies [30,31] show that three distinct configurations need to be considered for an acetophenone molecule adsorbed on clean Si(001) at low and room temperatures. The optimized atomic structures of the three adsorption geometries are shown in Figs. 2–4 while the details of the calculated structural parameters of the adsorbed configurations, as

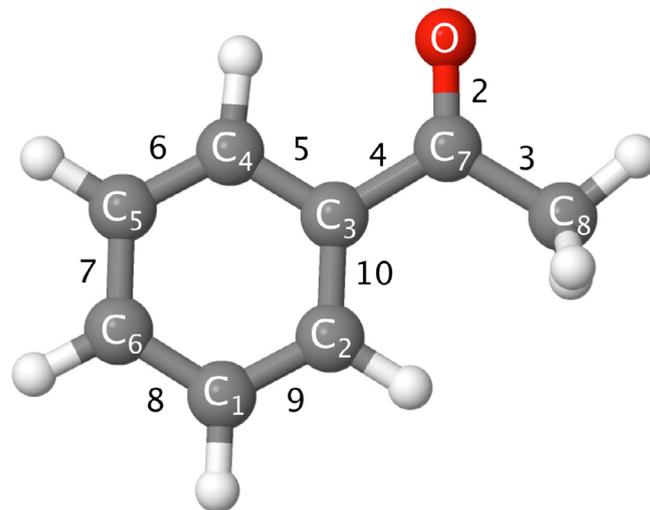


Fig. 1. Atomic structure of a gas phase acetophenone molecule (for structural details see Table 1).

well as the molecule in the gas phase (shown in Fig. 1), are presented in Table 1.

The configurations shown in Figs. 2–4 describe the dissociative adsorption of acetophenone with one H atom shifted from the molecular methyl group (CH<sub>3</sub>) to the Si substrate (for details of the kinetically and thermodynamically preferred adsorption and reaction scenarios see Ref.31). Our total energy calculations show that configuration C is by 1.19 eV and 1.23 eV energetically more favorable than configurations A and B, respectively, while configuration A is just by 0.04 eV more stable than configuration B, in good agreement with the published results [31]. It should be noted that despite the large differences in the calculated formation energies among the calculated structures, all considered configurations were observed experimentally – configuration C dominates the features observed at room temperature, while configurations A and B can be assigned to the features identified in the low temperature STM experiment [30,31].

### 3.2. Modifications of Si(001)-c(4 × 2) induced by the adsorption of acetophenone

In configurations A and B the Si dimers that are in direct contact with the adsorbed molecule (dimers a, b, c and d in Figs. 3 and 4) have their bond-lengths increased and their buckling angles reduced with respect to the corresponding values calculated for bare Si(001) (see Table 1; Si dimer bond length and buckling angle on clean Si(001) are calculated to be 2.34 Å and 21.17°, respectively). The obtained data presented in

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