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# First-principles investigation of CO adsorption on Pt/Ge(001)-(4 × 2)

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ABSTRACT

The electronic structure of the Pt-modified Ge(001) surface with adsorbed CO molecules is studied by means of total-energy calculations within the density-functional theory. The potential energy surface of the structure is calculated and the preferable position for CO adsorption is determined. The CO molecule is found to adsorb atop the Pt wires, and to lead to the opening of a small band gap. The CO adsorption does not heavily affect the substrate morphology.



## 1. Introduction

One-dimensional (1D) electronic systems are currently intensively investigated because their physics is rather different from the two- or three-dimensional cases [1,2]. Apart from the urgent technological need to understand and predict which properties may be met upon further size reduction, the research of nanowires is extremely interesting from a fundamental point of view. Lack of precise information on the conditions of the electric conductivity and its dependence on the atomic structure of nanowires initiates numerous theoretical researches in this field. Existing experimental techniques nowadays permits to fabricate nanostructures of atomic-scale dimensions, but it is still difficult to control the atomic geometry of such structures. One of the crucial points is the adsorption of foreign atoms and molecules, which may drastically change the electronic properties and, consequently, the conductance in the case of metallic wires [3]. Scanning tunneling spectroscopy does not allow to determine the effect of gas adsorption on metal clusters, as the number of adsorbed molecules and their adsorption sites are usually unknown [4]. To investigate the modification of the structural and electronic properties of the wires during the adsorption of molecular gases, theoretical simulations are necessary. Pt-nanowires on a Ge(001) surface have recently gained the attention of the scientific community as promising candidates for molecular electronic applications. In this context Pt-nanowire on the Ge(001) [5] is an interesting model system that may allow studying electron transport modifications by foreign atoms and molecules. Furthermore, the capability of Pt-nanowires to adsorb molecules may open a way for the creation of one-dimensional molecular chains. In this framework, CO seems to be the ideal candidate, due to its sticking probability, which is low for Ge and high for Pt. However, the question about the nature of the Pt-nanowires seems not to be completely settled. Gürlü et al. [6] and Öncel et al. [7] describe two types of terraces (called $\alpha$ and $\beta$ terraces) on the Ge(001) surface modified by Pt. According to their description, dimerized Pt atoms on the $\beta$ terraces form hundred nanometer long nanowires, which appear to be kink and defect free. The ridges on the Ge surfaces were accordingly interpreted as Pt-nanowires. Stekolnikov et al. [8] used a combination of total-energy calculations, electronic-structure studies and scanning tunneling microscopy (STM) to identify the one-dimensional structures observed on the reconstructed Pt/Ge(001) surface. According to their model, Pt–Ge bonds are favored versus Pt–Pt ones, and Pt induced Ge chains are formed instead of Pt-nanowires. The proposed tetramer–dimer chain model is able to explain the change from dimer-like to monomer-like STM features with decreasing tunneling bias and the subtile asymmetry observed in the experimental data. In our work we accepted the tetramer–dimer chain model, which we used as basis for the investigation of the CO adsorption on Pt/Ge(001). Recently Vanpoucke and Brocks [9] investigated theoretically Pt–Ge surfaces with different reconstructions. By comparison of their model with STM images, they could identify the exact geometry of the $\beta$ terraces and calculate their electronic structure. In this work we have simulated the

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Ge(001) surface modified by Pt in order to reveal the structural and electronic characteristics of the Pt chains and their modification by CO. At first the possible atomic configurations of Pt induced chains on the Ge surface were analyzed and structural optimization of such nanowires was performed. Then the influence of defects, notably CO molecule, on the structural properties of such nanowires was investigated. The potential energy surface (PES) of the structure, which gives an idea of the preferable absorption sites for the CO molecule, was calculated, and the electronic structure of the system determined.

## 2. Computational details

The total-energy calculations were performed within the density-functional theory (DFT) in the framework of the local density approximation (LDA) with projector-augmented waves (PAW) as implemented in VASP [10]. During the relaxation procedure the energy cut-off was set to 400 eV and a $2 \times 4 \times 1$ grid of Monkhorst–Pack points was used. Calculation of electronic properties was performed on the $4 \times 8 \times 2$ mesh of $k$-points.

The surface configuration and the Pt atomic positions were taken similar to the structural model proposed in Ref. [8]. This corresponds to $4 \times 2$ unit cell of germanium slab composed of eight Ge monolayers, which on turn corresponds to a slab width of 0.85 nm approximately, with two Pt atoms adsorbed onto the top. In the case of initial germanium slab all dangling bonds from both surfaces were terminated with hydrogen in order to avoid their influence on neighbouring slabs. In the case of structures with adsorbed atoms on top, only the bottom of germanium slab was terminated with H. The lattice constant of 0.56 nm was used. At the initial step of germanium slab relaxation, the Ge–H distance was taken to be 0.15 nm. The vacuum region was chosen of sufficient thickness to preserve the alternating slabs from mutual interaction. The preferable position of CO within the $4 \times 2$ cell was analyzed taking into consideration the possible orientation of the

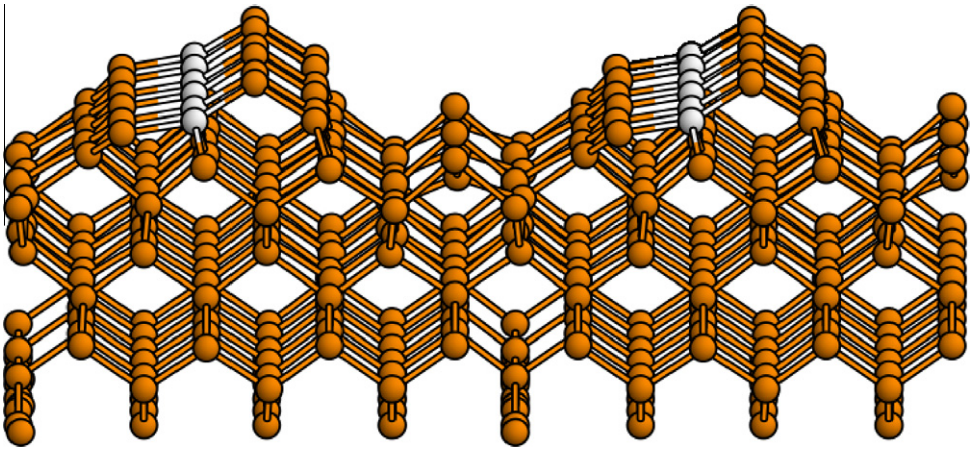

**Fig. 1.** Optimized atomic configuration of the clear Pt/Ge(001) surface. White atoms are Pt, darker atoms Ge.

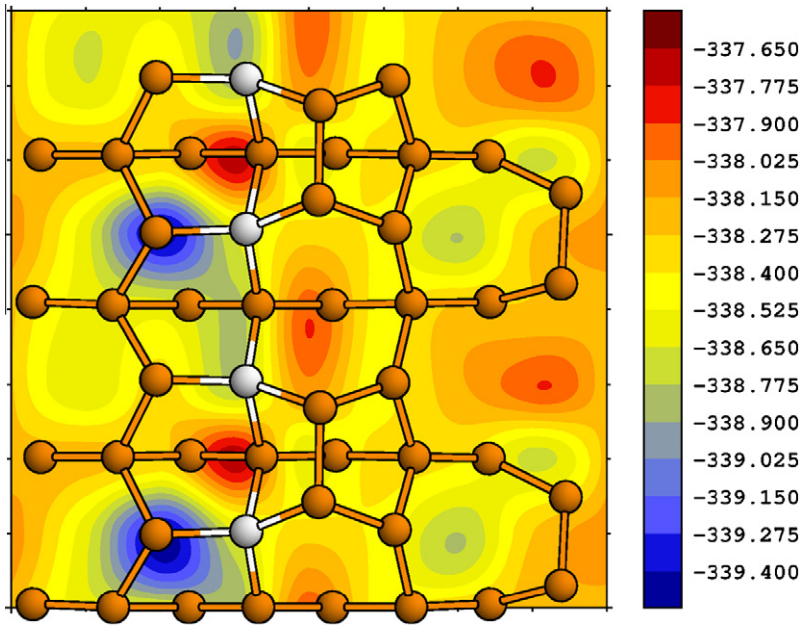


**Fig. 2.** Adsorption energy surface of Pt/Ge(001) structure with the adsorbed CO molecule. The energy is indicated in eV. Dark balls represent Ge atoms, light balls Pt atoms. The CO molecule is not shown.

molecule when either carbon or oxygen atom is closer to the surface. The Pt 5*d* electrons were considered as valence, since they play a central role in the Pt–Ge bonding [8].

## 3. Results

After relaxing the substrate (shown in Fig. 1), we have determined the favored adsorption site for the CO molecule on the considered structure. Therefore in a first step we have calculated the related PES, which gives an approximate idea of the stable adsorption site and a map of the different energy minima on the surface. The PES is calculated constraining the *x* and *y* coordinates of the lower atom of the molecule and allowing everything else to relax. We have evaluated the adsorption energy for 32 possible positions on the top of the structure (see Fig. 2). The PES of this system is strongly corrugated and demonstrates clear minima and maxima of the adsorption energy. The total energy minimum occurs when the CO molecule occupies a slightly titled position between a lower lying germanium atom and a Pt atom (dark region in Fig. 2).

Subsequently, we have determined the optimal configuration for a single CO molecule adsorbed on Pt the nanowire. Thereby, we start with the molecule at the favoured adsorption site as obtained from the PES calculation, but let the molecule and the surface now relax without any constraints. The CO molecule slightly moves toward the Pt atom. The relaxed geometry, with the molecule closer to the Pt atom, is shown in Fig. 3. This confirms the low sticking probability of CO to Ge compared with Pt. We find the CO molecule to adsorb with the C atom pointing to the wires. We have obtained the following bond lengths: $d$(Pt–C) = 0.19 nm, $d$(C–O) = 0.116 nm, which are close to $d$(Pt–C) = 0.18 nm, $d$(C–O) = 0.115 nm obtained in [11] and close to the experimental distance in CO gas (0.113 nm) [12]. The adsorption energy, estimated by

$$E_{\mathrm{slab}}(\mathrm{Pt@Ge} + \mathrm{CO}) - E_{\mathrm{slab}}(\mathrm{Pt@Ge}) - E_{\mathrm{free}}(\mathrm{CO})$$

has been calculated to be 2.8 eV. The CO chemisorption at Pt-modified Ge(001) has been investigated experimentally (see Ref. [3]). However, the interpretation of the experimental results was completely based on the Pt-nanowires model of Refs. [6,7], and the CO molecules were found to bind at the bridge position of the Pt-dimers. The Pt chains model of Ref. [8] accepted in this work substantially differs from the previous model so that our results are not directly comparable with the cited experimental findings.

The analysis of the electronic properties of germanium slab is complicated by the particle in a box effect. Instead of the gapless band structure, which is usually obtained within DFT calculations of germanium bulk [13–15], due to the quantum confinement effect the structure investigated here is a direct-gap semiconductor with the gap value of about 0.9 eV. That coincides well with the results obtained in [16] for germanium quantum films. The formation of the Pt wires on the Ge surface leads to the appearance of new surface states and to an increased number of states in the band gap region, as can be seen from the DOS in Fig. 4. This is in agreement with the calculations of Ref. [9]. However, the adsorption of carbon monoxide widens the band gap and changes the dispersion of valence bands restoring the semiconducting properties

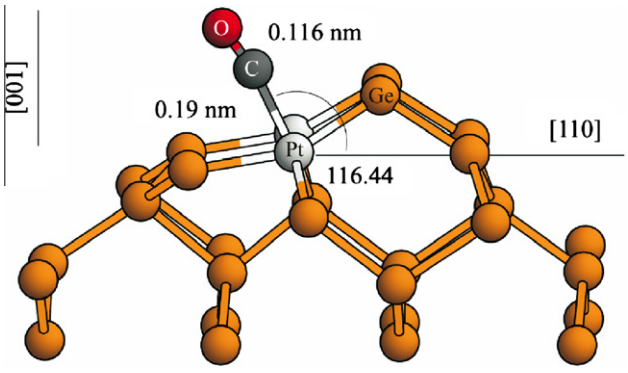


**Fig. 3.** Optimized atomic configuration of the Pt/Ge(001) surface with the adsorbed CO molecule.

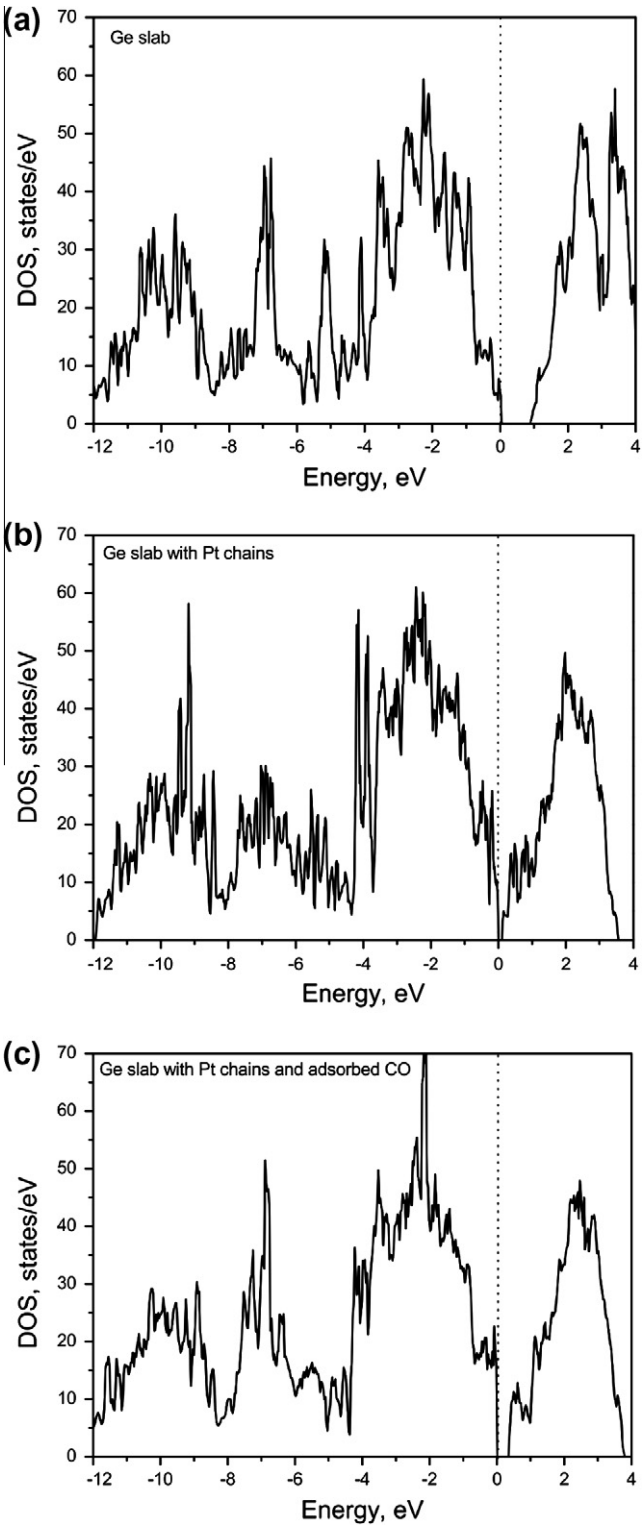


**Fig. 4.** Total density of states of the germanium slab with 4 × 2 symmetry: initial germanium surface (a); platinum modified surface (b); platinum modified surface with adsorbed CO molecule (c). The energy zero corresponds to the Fermi level.

of the system. The small band gap of approximately 0.1 eV calculated for the germanium slab with platinum wires is beyond our numerical accuracy. It does not necessarily indicate the semiconducting nature of the system, whereas the gap widening up to approximately 0.2 eV upon CO adsorption permits us to conclude the general tendency of gap transformation. Thus, the presence of the CO molecule modifies the band structure of Pt induced chains, in a similar way as in the case of CO adsorption on Au chains in Ref. [4]. Considerable changing of the germanium substrate under CO adsorption does not occur: carbon monoxide affects mostly the neighboring Pt atoms [17].

## 4. Conclusion

In conclusion, we have performed DFT-LDA calculations for the CO adsorption on Pt/Ge(001) and found that the molecule tends to adsorb on the top of Pt atom, but it is slightly titled from surfaces normal. The molecular adsorption leads to a gap opening in the surface band structure and does not heavily affect the substrate geometry.

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