МАТЕРИАЛЫ

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AB INITIO INVESTIGATION OF CO ADSORPTION ON SELF-ASSEMBLED PT NANOWIRES ON Ge(001)

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Electronic structure of 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 preferable position for CO adsorption is determined.

Keywords: CO molecule, self-assembled Pt nanowires, electronic properties, potential energy surface.

Introduction

The ever-shrinking feature size in integrated circuits combined with the ability to manipulate atoms and molecules with increasing precision is driving huge research efforts into the properties of atomic-scale nanowires. The 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 what properties may be met upon further size reduction, the nanowire research is extremely interesting from a fundamental point of view. There was no precise information available on the conditions for electric conductivity and its dependence on the atomic structure of nanowires.

Pt nanowires on a Ge(001) surface have recently gained the attention of the scientific community as promising candidates for molecular electronic applications. Pt nanowires on the Ge(001) [3] are an interesting model system in this context that may allow studying electron transport modifications by foreign atoms and molecules [4]. Furthermore, the possibility of Pt nanowires to adsorb molecules may open the way for the creation of one-dimensional molecular chains. In this framework, CO seems to be the ideal candidate, due to its affinity and sticking probability, which are low for Ge and high for Pt. However, the question about nature of the Pt nanowires seems not to be completely settled. Gurlu [5] and Oncel *et al.* [6] describe two types of terraces (called α and β terraces) on the Pt modified Ge(001) surface. According to their description, dimerised Pt atoms on the β terraces form hundred nanometer long nanowires, which appear to be kink and defect free. Stekolnikov *et al*. [7] instead proposed that the structures observed on the reconstructed Pt/Ge(001) surface are Pt induced Ge chains instead of Pt nanowires.

In this work we simulate from first principles the Pt modified Ge(001) surface, in order to reveal the structural and electronic characteristics of the Pt chains and its modification by CO. As a first step possible atomic configurations of Pt chains on the Ge surface were analyzed and atomic relaxation with structure optimization of such nanowires was performed. Based on the structural model proposed in [7] the information about possibility of formation of Pt low-dimensional chains on the germanium surface with (001) orientation was obtained. In a second step 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 preferable absorption sites for CO molecule on Pt chains, was calculated.

Details of calculations

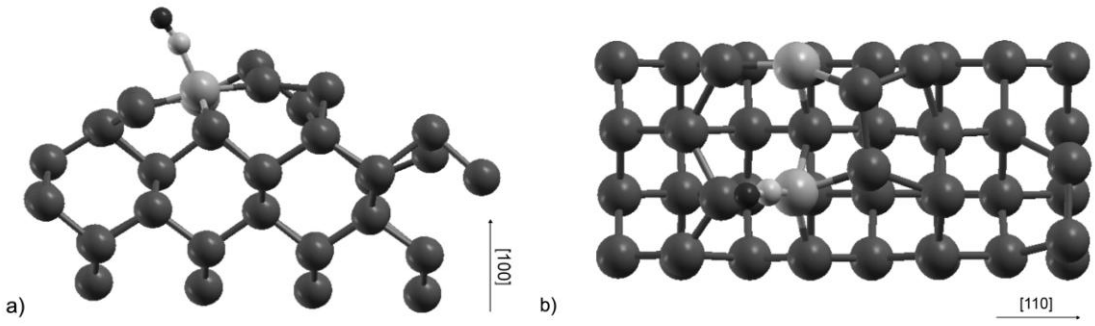
The total-energy calculations were performed within the density-functional theory (DFT) in the framework of the generalized gradient approximation (GGA) using the VASP implementation [8] with projector-augmented wave (PAW) method with the purpose to determine and verify the wire geometry.

We have analyzed 32 possible variants of CO molecule adsorption on the Pt reconstructed Ge surface. First we relaxed the known structure [7], which was presented by 8 Ge monolayers with 2 Pt atoms, adsorbed onto the top, within 4x2 unit cell. The bottom of the slab was terminated with hydrogen in order to avoid influence of dangling bonds. The preferable position of CO within the 4x2 cell was analyzed taking into consideration possible orientation of molecule when either carbon or oxygen atom is closer to the surface. Particular attention was paid to the role of the 5d Pt electrons, which, as proposed by Stekolnikov et al. [7] play a central role in the Pt-Ge bonding.

Results

As it was expected, we have found that carbon atom is closer to the surface and the CO molecule occupies on-top site above Pt atom. This can be easily explained by the fact of low affinity to Ge, which is, in turn, higher for Pt. We have obtained the following bond lengths: d(Pt-C)=1.9 Å, d(C-O) =1.16 Å, which are close to d(Pt-C)=1.8 Å, d(C-O)=1.15 Å obtained in [9] and close to experimental distance in CO gas (~1.14 Å).

Optimal configuration with one CO molecule, adsorbed on Pt nanowire, was established (Fig. 1). We determined the PES for CO molecule adsorbed on the considered structure and evaluated adsorption energy for 32 possible positions on the top of the structure (Fig. 2). The PES of this system is not very flat due to the roughness of the surface and demonstrates clear minima and maxima of total energy for different adsorption sites. The total energy minima occur when CO molecule occupies the slightly titled position on top of the platinum atom.



a *b*

Fig. 1. Optimized atomic configuration of Pt/Ge(001) structure with adsorbed CO molecule: *a*) side view; *b*) top view

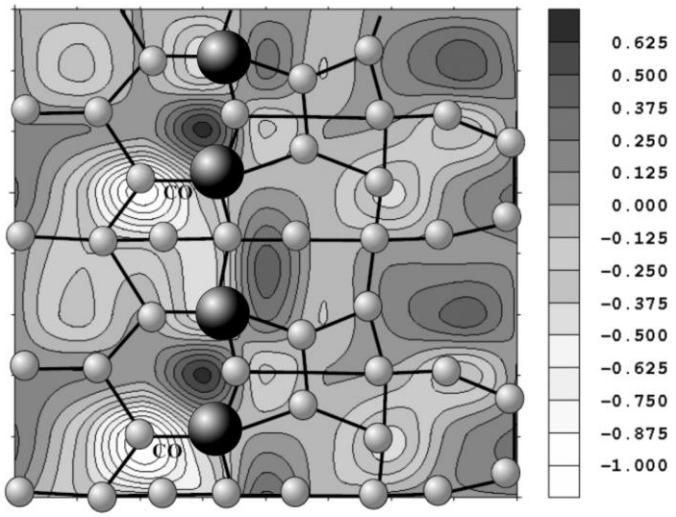


Fig. 2. Adsorption energy surface of Pt/Ge(001) structure with an adsorbed CO molecule. Energy is indicated in eV. Gray balls represent Ge atoms, black balls — Pt atoms. CO molecule is not shown

Conclusion

The performed work was aimed at understanding of precise atomic structure and electronic properties of self-organized atomic-scale nanowires formed by Pt on Ge(001) surfaces, and investigation of the impact of adatoms and defects on the structural properties of these wires. The information about structure and properties of such nanowires is necessary for design of new nanoelectronic devices as they may find application as atomic-scale interconnections. It was established that CO molecule tends to adsorb on the top of Pt atom, but it is slightly titled from surface's normal. For evaluation of the changes in conductivity of the system further transport calculations are necessary.

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