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Confined Ge–Pt states in self-organized Pt nanowire arrays on Ge(001)

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Abstract. By means of band structure calculations within the density functional theory and the generalized gradient approximation, we investigate the electronic structure of self-organized Pt nanowires on the Ge(001) surface. In particular, we deal with a novel one-dimensional surface state confined in the nanowire array and clarify its origin. Due to large Pt contributions, the novel state is rather a mixed Ge–Pt hybrid state than a confined Ge surface state. Moreover, we compare our results to data from scanning tunneling microscopy.

PACS. 73.20.-r Electron states at surfaces and interfaces – 73.20.At Surface states, band structure, electron density of states

Because of a wealth of extraordinary physical properties, self-organized nanowires recently attract great attention. Of special importance are self-organization phenomena on semiconductor surfaces, due to a wide field of possible technological applications. For the Ge(001) surface, for example, Au growth comes along with a large variety of ordering processes as a function of the Au coverage and growth temperature [1,2]. Moreover, adsorption of Pt atoms results in well-ordered chain arrays after high-temperature annealing [3]. These spontaneously formed Pt nanowires are promising with respect to their thermodynamical stablity, regularity, and length, which reaches up to several hundred nanometers. In order to obtain detailed insight into their physical properties and the self-organization process, exact knowledge about the surface electronic states is mandatory, which we address in the present paper.

A one-dimensional electronic state on the Pt-covered Ge(001) surface has been discovered by Oncel et al. [4]. Using scanning tunneling microscopy, the authors have measured spatial maps of the differential conductivity and afterwards calculated from these data the local density of states (DOS). At a temperature of 77 K and for a nanowire spacing of 1.6 nm, they find an unexpected DOS peak some 0.1 eV above the Fermi level. They argue that this electronic state is located in the Ge trough between the Pt nanowires and, therefore, attribute it to a confined Ge surface state. However, the Ge(001) surface is known to be subject to strong hybridization under Pt coverage [5]. For this reason, we subsequently investigate the electronic structure of the Pt-covered Ge(001) surface by means of electronic structure calculations based on density functional theory. The band structure results discussed in the following rely on a fully relaxed supercell of the Ge–Pt surface, where the distance between neighbouring Pt nanowires has been set to 1.6 nm in order to prepare for a comparison of our first principles findings to the experimental DOS.

We use the generalized gradient approximation (GGA) implemented in the full-potential linearized augmented-plane-wave WIEN2k code [6], which is known for a very high capability in dealing with surfaces/interfaces [5,7]. The exchange-correlation potential here is parametrized according to the Perdew-Burke-Ernzerhof scheme. Our data is based on a supercell of the cubic Ge unit cell consisting of a $c(4 \times 2)$ reconstructed surface array and extending two unit cells perpendicular to the surface. The formation of Pt chains on Ge(001) is accompanied by the partial breakup of the Ge surface dimers [3]. For obtaining a useful starting point for the structure optimization we thus start from the clean Ge surface, leave away each fourth row of upper Ge dimer sites, and place Pt atoms in the trough next to that row. Finally, we assume convergence of the structure optimization when the surface forces have decayed below a threshold of $5\,\mathrm{mRyd}/a_B$.

Figure 1 shows partial Pt 5d and Ge densities of states as resulting from our electronic structure calculation. As an example, we address the DOS of the upper dimer Ge site. However, the following discussion does not depend on this choice, as similar results are obtained for all Ge surface sites. For comparison, Figure 1 includes the upper dimer Ge DOS for the clean Ge(001) surface without Pt nanowires [8]. Confirming the findings of Oncel et al. [4],

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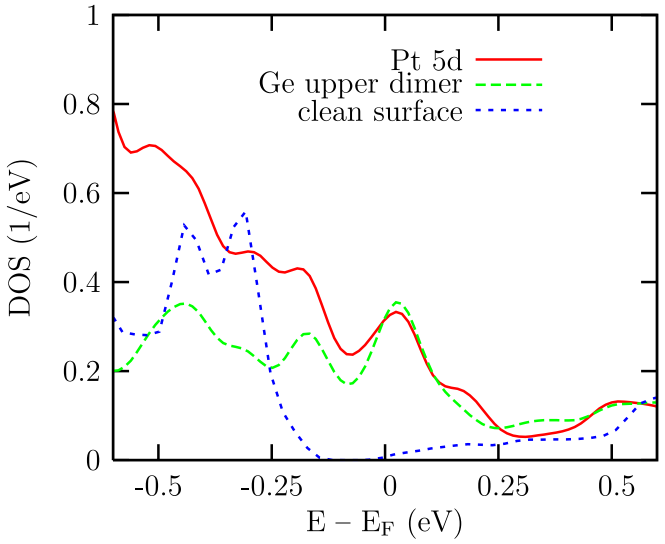

Fig. 1. (Color online) Partial Pt 5*d* and Ge densities of states (per atom) in the vicinity of the Fermi energy. The Ge DOS refers to the upper dimer site and is shown both for a clean Ge(001) surface and a surface covered with Pt nanowires. For convenience, the Pt 5*d* DOS is downscaled by a factor 1/2.

Figure 2b, for the Pt-covered surface a distinct structure appears in the Ge DOS just above the Fermi level, which we therefore ascribe to the novel electronic state under consideration. In the theoretical DOS, it is found at an energy of some 0.05 eV, rather than at the experimental value of 0.1 eV. Amazingly, the 0.05 eV peak reappears in the Pt 5*d* DOS with a very similar shape. While the Ge DOS in Figure 1 is normalized with respect to the number of atoms contributing, the Pt 5*d* DOS additionally has been downscaled by a factor 1/2. As a consequence, a significant amount of the spectral weight in the vicinity of the Fermi energy has to be attributed to the Pt nanowires. Furthermore, careful analysis of the band structure reveals that mainly two electronic bands of mixed orbital character give rise to the DOS structure around 0.05 eV. Such a strong hybridization clearly points at significant Ge–Pt interaction. Figure 2 depicts the band structure in the relevant energy range, where either the Ge or Pt 5*d* contributions to the states are highlighted by means of the point size. The representation refers to the first Brillouin zone, and the direction parallel to the surface plane and perpendicular to the nanowires. A tiny band gap of approximately 0.03 eV is observed in Figure 2, reflecting the fact that the conductivity of the Pt-covered Ge(001) surface is basically connected to the nanowire formation.

While the existence of a novel surface electronic state is confirmed, our band structure data spoil an interpretation in terms of a confined Ge surface state. Instead, as large Pt admixtures are due to strong Ge–Pt hybridization, the state must originate from both the Ge surface and the Pt nanowires. Supporting our line of reasoning, scanning tunneling microscopy (STM) data, as obtained by Schäfer et al. [9], show that the Pt conduction bands are seriously modified by the interaction with the Ge substrate. For comparison, we present a simulted STM image in Figure 3. The image indicates a remarkable dimerization of the Pt valence states, which are seen in the very center of Figure 3, running from top to bottom. However, contradicting the experiment, this dimerization does not vanish for states close to the Fermi level. Modelling the surface energy levels in terms of a quantum mechanical particle in a well, as proposed in [4], does not suffer from our interpretation in terms of mixed Ge–Pt states. Exactly the same applies to the fact that the state gradually fades away close to structural defects of the nanowires or the substrate. In contrast, the experimental observation of an almost

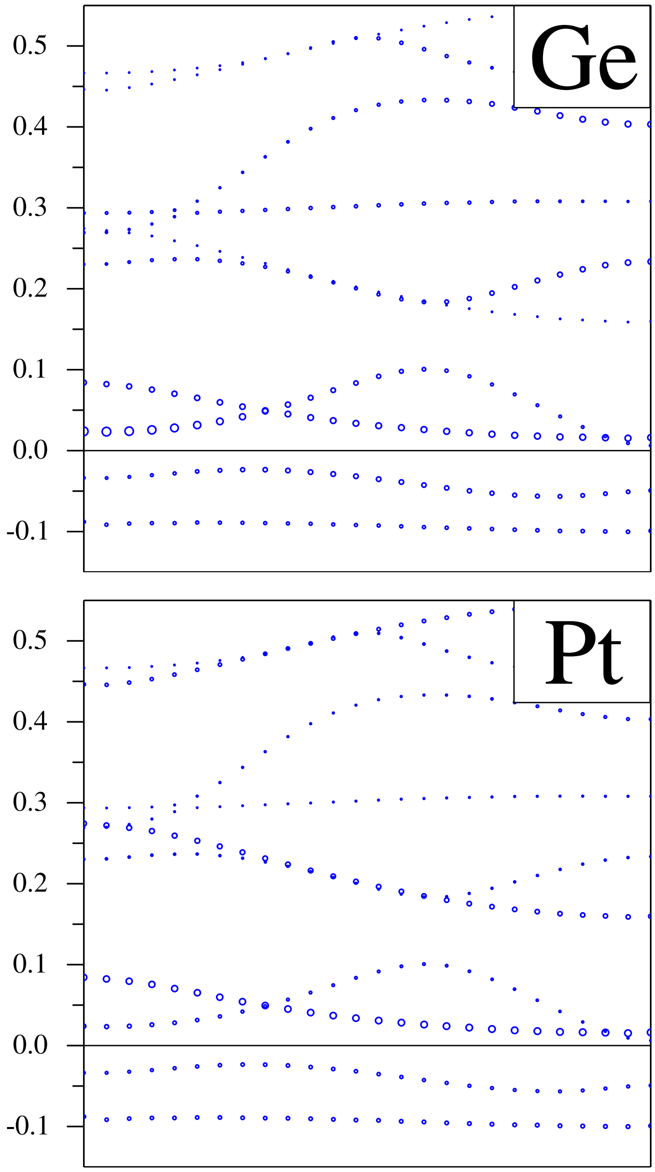

Fig. 2. (Color online) Weighted electronic bands highlighting Ge and Pt 5*d* contributions via the size of the circles drawn for each band and **k**-point. Covering the first Brillouin zone, the representation refers to the direction perpendicular to the Pt nanowires in the surface plane.

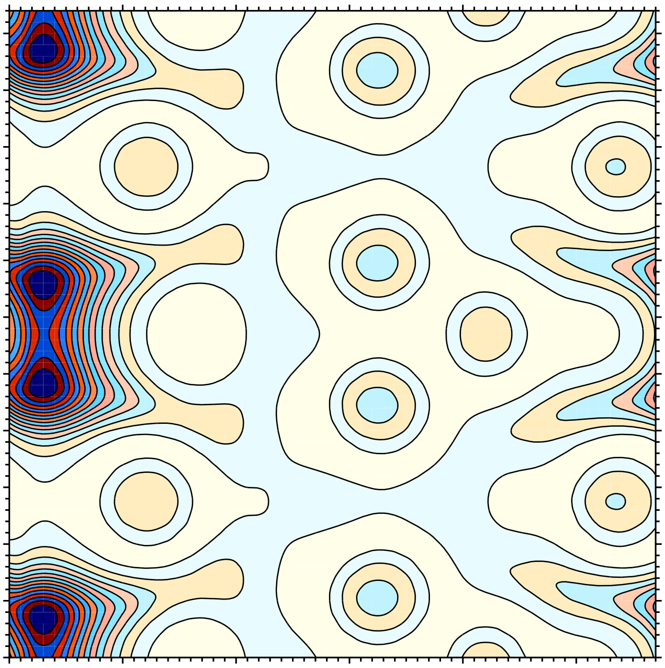

Fig. 3. (Color online) Simulated STM image, based on the occupied DOS in the energy range from −1 eV to the Fermi level. The valence states of the Pt chains (center of the figure, running from top to bottom) reveal a distinct dimerization.

perfect localization within the Ge trough is puzzling because of the large Pt admixtures. However, the simple shape of the band with the largest Ge–Pt hybridization in Figure 2 indicates that the novel surface state is captured by the classical Kronig–Penney model. Thus, it is well described in terms of a non-localized Ge–Pt state confined in the periodic potential of the nanowire array.

In conclusion, we have presented first principles band structure calculations for the Pt-covered Ge(001) surface and studied the surface electronic structure. In particular, we have focused on a novel electronic state, located right above the Fermi energy, which is not found for the clean Ge(001) surface. Contradicting a previous experimental prediction, our data show that this state does not originate from simple confinement of a regular Ge surface state. For an adequate interpretation of the experimental DOS it is essential to account for strong Ge–Pt hybridization, which is not surprising because interaction between the substrate and the adsorbate is expected to be of great importance for the adsorption process [5,10].

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