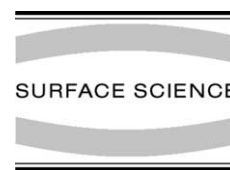




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Adhesion of metal on metal. The Pt on Co case

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Abstract

The adhesion of Pt overlayers in pseudomorphic epitaxy on hcp Co(0001) and fcc Co(100) was investigated with first-principles calculations. This was compared to the adhesion of the Pt surface layers on Pt(111) and Pt(100). We show that adhesion can be analyzed by taking into account the interplay between the chemical and structural properties at the interface. The free Pt planes with the bulk Pt–Pt distance are submitted to tensile stress which can be relaxed by 6.6% and 9.1% contraction for the (111) and (100) symmetries respectively. This results in equilibrium interatomic distances which are not far from that of the Co substrate. Consequently the stress energy in a pseudomorphic Pt monolayer on a Co substrate is lower than the stress energy of pure Pt(111) or Pt(100) surfaces. However, this is at the expense of the Pt chemical reactivity towards the Co substrate. This is in agreement with the general dependence between chemical reactivity and stress of a metal surface.   2001 Elsevier Science B.V. All rights reserved.

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During the last decade, the physical and chemical properties of model surfaces obtained by metal deposition on a metal substrate has attracted much attention [1]. Most of them reveal high specificities due to the interaction between the components. In the case of Pt deposition on Co(0001), STM imaging showed that Pt grows as monatomic-thick islands in the submonolayer coverage range [2]. Although no atomic resolution could be obtained, the use of several techniques (Low energy electron diffraction, LEED; X-ray and UV photoemission spectroscopies, XPS and UPS) permitted to propose a consistent model of the islands structure

with a symmetry similar to that of a fcc (111) plane and Pt–Pt distances shorter than in pure Pt. CO adsorption on these surfaces was used to check their chemical properties [3]. The decrease of the CO adsorption energy by about 40% on the Pt islands with respect to the pure Pt(111) surface was in good agreement with a strong reduction of the Pt–Pt distance [4].

In order to improve our knowledge of the Pt/Co system, models formed by pseudomorphic Pt monolayers deposited on hcp Co(0001) or fcc Co(100) substrates were examined with use of first-principles calculations. As we are mainly interested by the chemical properties of the Pt layers, we will focus our attention here on the Pt–substrate bonding. Moreover, we will take as references the homogeneous systems formed by the same Pt monolayers in interaction with Pt(111) or

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Pt(100) unreconstructed substrates. For a given system, the initial state before Pt adhesion on the substrate was formed by a relaxed Pt monolayer of the proper symmetry and the infinitely separated substrate. The final state consisted of the Pt overlayer in pseudomorphic epitaxy on the substrate separated by the distance corresponding to the lowest total energy. The energy released between these two states is taken as the adhesion energy. Clearly, the Pt–Pt distance varies between the initial and final states of the system. Consequently, we can decompose the evolution to adhesion in two steps. The first one is simply the change of the Pt–Pt distance in the free Pt monolayer to the interatomic distance in the substrate surface plane. In the second step, this constrained Pt monolayer is approached from infinity to the substrate. The energy involved in the first step checks the strain energy suffered by the Pt monolayer in the final state. The energy released in the second step probes the strength of the Pt–substrate chemical interaction. Hereafter, we will designate it as the separation energy of the Pt monolayer from the system.

The models used in our calculations were semi-infinite slabs separated by 10 Å vacuum in the direction perpendicular to the surface. We considered slabs formed by one Pt layer and three substrate layers (either Co or Pt). When the Pt(111) plane was assembled with the Co planes, these latter planes were in compact stacking and the Pt layer was deposited in epitaxy so that the overall slab had the hcp geometry. For deposition of the Pt(100) monolayer on Co we considered the fcc symmetry. In both cases, the in-plane cell parameter was 2.50 Å. Isolated Pt planes with the (111) or (100) geometry were also considered. In that case, the unit cell parameter, i.e. the Pt–Pt distance was contracted down to $\approx 12\%$ in order to check their ability to adopt the same parameter as a substrate underneath. Our calculation technique gives 2.807 Å as the Pt–Pt distance for unconstrained bulk Pt that is taken as a reference. The same theoretical value was obtained by other authors [5] using a similar method than ours. This should be compared to the experimental value which is 2.775 Å. For bulk Co, the experimental Co–Co distance is 2.507 Å.

Nonlocal gradient-corrected density functional (PW91) calculations [6] were used to determine the structural and energetic results presented in this letter. Magnetism was not considered in our calculations. Considering the low level of magnetic energy, this should not perturb significantly our results. Ion cores were described by ultrasoft pseudopotentials [7]. The valence states were expanded with a plane wave basis up to a kinetic energy cutoff of 500 eV. The Brillouin zone was sampled at 128 special k -points with a $(16 \times 16 \times 1)$ grid. Special attention was paid for the isolated plane calculations which involved large variations of the unit cell parameter. The convergence was checked from 162 k -points up to 288 k -points. We found that the energy variations did not exceed 2×10^{-3} eV and that the energy differences involved in our calculations had an uncertainty smaller than 10^{-3} eV. Consequently, these calculations were performed using 162 k -points on a $(18 \times 18 \times 1)$ grid.

Fig. 1 shows the energy change of the free (111) and (100) planes when the Pt–Pt distance was modified. In the two curves the energies have been referred to the minimum located at 2.62 and 2.55 Å for the (111) and (100) monolayers respectively representing 6.6% and 9.1% contraction from the bulk equilibrium distance. This put in evidence that any surface plane of a pure substrate is submitted to a tensile stress [8]. The lower the coordination is, the shorter the equilibrium interatomic distance. We report in Table 1 the energy increase resulting when the equilibrated Pt monolayers are contracted (expanded) to fit the in-plane interatomic distance of Co (Pt). We note that the (tensile) strain energies suffered by the Pt surface layer of Pt(111) and Pt(100) are higher than the (compressive) strain energies on a Co substrate of similar symmetries. This suggests that, as long as the strain energy only is considered, the heterogeneous system is favored against the homogeneous one. Actually, for Pt(100) the Pt–Pt distance of the relaxed Pt free monolayer is so close to the interatomic distance of the Co(100) substrate that the strain energy amounts to 0.023 eV only. On the contrary, the highest energy increase is obtained for the same symmetry with the bulk Pt–Pt distance. This is in good agreement with the tendency

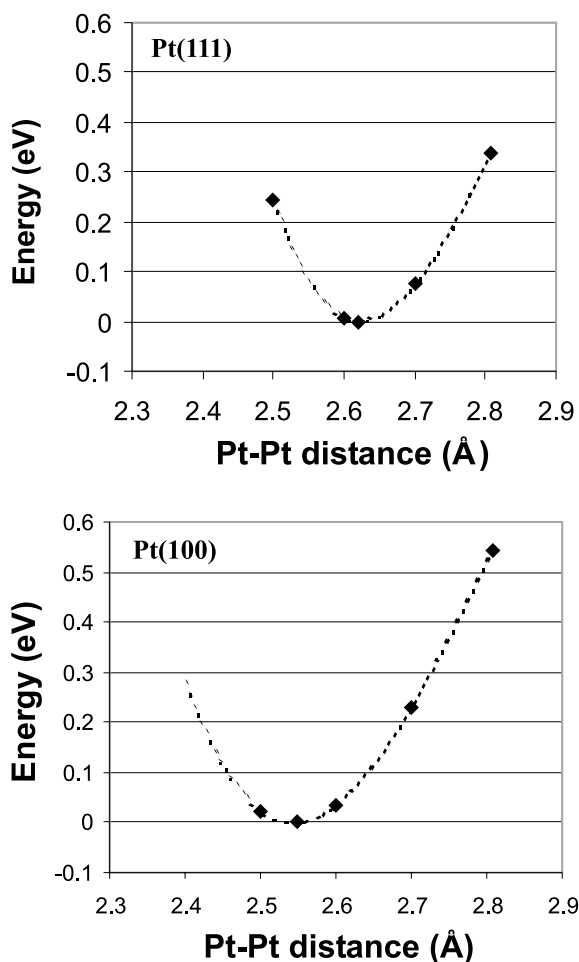


Fig. 1. Energy change of the free (111) and (100) Pt layers versus the Pt–Pt distance. The dashed curve is a third degree polynomial used as a guide for the eyes.

Table 1

Energy increase (eV atom^{-1}) when the equilibrated Pt(111) and Pt(100) free monolayers are expanded or contracted to the interatomic distance of the Co and Pt substrates

Substrate	Interatomic distance (Å)	Energy increase (eV atom^{-1})	
		Pt(111)	Pt(100)
Co	2.50	0.242	0.023
Pt	2.807	0.338	0.542

of the Pt(100) surface for reconstruction to a higher atomic density [9], which helps to relax the tensile stress.

Table 2

Separation distance (d) between the Pt overlayer and the first substrate layer at the lowest energy of the system

Substrate	d (Å)		d' (Å)	
	Pt(111)	Pt(100)	Pt(111)	Pt(100)
Co	2.281	1.970	2.699	2.647
Pt	2.295	1.935	2.810	2.772

d' is the distance between a Pt atom in the overlayer and a nearest next-neighbor in the first substrate layer below.

Table 3

Separation and adhesion energies for Pt overlayers in epitaxy on Co or Pt

Overlayer	Separation energy (eV atom^{-1})	Adhesion energy (eV atom^{-1})
<i>Co-substrate</i>		
Pt(111)	1.056	0.814
Pt(100)	1.664	1.641
<i>Pt-substrate</i>		
Pt(111)	1.325	0.986
Pt(100)	2.031	1.489

We now consider the results of our calculations when the constrained Pt monolayer is in pseudomorphism on the Co or Pt substrates. We give in Table 2 the distance (d) between the Pt overlayer and the first substrate plane corresponding to the lowest energy. The adhesion and separation energies as defined above are given in Table 3.

We will first discuss the separation energies. In every case, they are significantly lower on Co than on Pt even if they remain substantial for the heterogeneous systems. However, it has been theoretically demonstrated [4] and experimentally checked [3] that a surface layer under compressive stress (as our Pt/Co models) is chemically less reactive than the same surface layer under tensile stress (as our Pt/Pt models). Therefore our present results are consistent with these references. Furthermore, we note that the separation energies are higher for Pt(100) than Pt(111) on both substrates. This is in line with the expectation that the less coordinated surface will be the most chemically reactive as a consequence of its poor cohesion energy.

We now examine the adhesion energies reported in Table 3. Of course, as the free Pt monolayer is

now taken in its relaxed initial state, the numerical values are always lower than the corresponding separation energies. However, we can see that the adhesion energies change less when going from the Pt substrate to the Co substrate than the corresponding separation energies. The reason is that the tensile stress energy for Pt/Pt is higher than the compressive stress energy for Pt/Co as already outlined in the discussion of Table 1. The most striking consequence is that the adhesion energy of Pt(100)/Co(100) is even higher than that of Pt(100)/Pt(100). This demonstrates that the Co(100) substrate stabilizes better the pseudomorphic Pt(100) monolayer than the Pt(100) substrate does. On the contrary, the Pt(111) plane is better stabilized on the Pt substrate than on Co(0001). The reason is that, in spite of an identical compression of the Pt–Pt bond in the two Pt monolayers, the (111) plane is less chemically reactive than (100) due to its higher coordination. Nevertheless, the Co(0001) substrate remains a good stabilizer of the Pt(111) monolayer. This last point is in qualitative agreement with semi-empirical calculations performed on the same system [10].

In conclusion, our calculations demonstrate that it is very important to take into account the interplay between the chemical and structural properties of a surface. This was used to under-

stand the adhesion properties of a pseudomorphic Pt overlayer on a Co substrate. Although the adhesion of Pt on Co is in the same range than the adhesion on a Pt substrate, we show that the two cases are different. The reason is that in the former case the compressive stress in the Pt monolayer lowers the chemical reactivity at the interface. In the latter case, the Pt surface layer under tensile stress is chemically more reactive.

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