

CO Adsorption on Co(0001)-Supported Pt Overlayers

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Abstract: the growth of Pt deposits on Co(0001) was followed by STM and XPS. The chemical reactivity of the resulting surface was checked by CO adsorption. Pt grows as dendritic islands on the Co terraces whereas forming stripes at the Co step edges. Annealing the sample has no apparent effect on the STM pictures. However, XPS suggests that a limited dilution of Pt in Co takes place. The adsorption of CO on the surface is drastically affected by the presence of Pt even for minute traces. The adsorption energy on the Pt areas is decreased by 40 %. The maximum coverage on the Co areas is also decreased. This indicates that Pt impurities diluted in Co have a high passivating power as a consequence of the induced electronic changes.

Keywords: adsorption, CO, Pt, Co, thin films.

Introduction

During the past decade bimetallic surfaces, either metal overlayers or surface alloys, have been the subject of a tremendous activity [1]. This is because this kind of systems exhibits original physical as well as chemical properties due to their structural and electronic features. Thus, PtNi surface alloys have showed catalytic activities that do not resemble those of their pure components [2, 3]. Ruban et al. [4] published a systematic study of the theoretical local electronic structure of pseudomorphic metal monolayers on various metallic substrates in connection with their chemical reactivity. They pointed out the importance of the d-band position on the adsorption properties. In a previous work, we studied the growth of Pt thin layers on Ni(111) [5] and Co(0001) [6]. The growth of monatomic-thick Pt islands on Co(0001) was observed by scanning tunneling microscopy (STM) [6]. The adsorption

properties of both systems were studied theoretically [7, 8] and experimentally [9]. We showed that the adsorption energy of CO on the Pt islands grown on Co(0001) was lower than on pure Pt(111) by about 40 %. This was attributed to the compressive in-plane stress suffered by the islands.

In this paper, we focus on the dependence of the morphology and the adsorption properties of the Pt/Co(0001) system with the thermal treatment performed before exposure. Actually, the metallic overlayers may be thermally unstable. In order to take advantage of their unique properties, it is determining that they are stabilized at their working temperature, as catalytic reactions are generally performed higher than room temperature.

Experimental

The experiments were performed in a vessel formed by three interconnected high-vacuum chambers. The working pressure was in the low 10^{-10} Torr range. The first chamber allows for low energy electron diffraction (LEED) observation of the sample surface. The central chamber is devoted to sample preparation and photoemission spectroscopy (XPS). It is equipped with a twin anode permitting the use of Al-K α and Mg-K α X-rays, and a hemispherical analyzer. Pt deposition from a resistively heated ribbon and CO exposures were also performed in this chamber. The third chamber permitted STM imaging of the sample with Pt-Ir tips. It was used to determine the overall surface morphology before and after Pt deposition. However, no atomic resolution could be obtained.

The sample was prepared by annealing and Ar-ions bombardment. The sample temperature was kept lower than 650 K in order to avoid the Co phase transition from hcp to fcc. C and O were the two contaminants detected at the surface. C could be entirely eliminated by the cleaning procedure. The residual O pollution was estimated to be lower than 5 % of a monolayer (ML). Pt was then deposited at room temperature at the approximate speed of 4×10^{-2} ML min $^{-1}$. The sample was then heated at 550 K for two hours. The Pt coverage $\theta(\text{Pt})$ was estimated from the Pt 4f peaks recorded by XPS.

CO exposures were performed using the following procedure. CO was admitted to interact with the sample at a pressure of 2×10^{-7} Torr at room temperature for 15 min. Then the pressure was decreased to 1.2×10^{-7} Torr and the photoemission spectra were recorded. The aim of this procedure was to approach saturation of the surface during the first pressure step and then to obtain readily the equilibrium coverage in the second step, minimizing any possible evolution during the recording time. In order to reduce the working time of the X-ray source at this CO pressure, the spectra were generally recorded with a poor resolution (pass energy of 50 eV). A better resolution (pass energy of 20 eV) was however used in specific cases.

Results and discussion

We present the results obtained after CO exposure. Prior CO interaction, the sample was or not submitted to annealing in the conditions described above. This gives two series of data hereafter called "as-deposited" or "annealed".

The freshly prepared surface was examined with STM before and after Pt deposition. Figure 1 gives some examples of the as-deposited (Pt coverage 0.12 ML) and annealed (Pt coverage 0.18 ML) surface. We can recognize the same features among the four images. Dendritic Pt islands appear on the Co terraces. Cross-section measurements show that they are 1 monolayer-thick. The clean Co(0001) surface was also examined using STM. The surface exhibited flat terraces several hundred Å wide, separated by monatomic or sometimes diatomic steps [6]. These steps were more or less linear at a scale length of ca 500 Å. On the contrary, the images reported in figure 1 show dendritic shapes along the step edges, similar to the island edges. Obviously, the step edges were modified by Pt deposition. Actually, most of the Pt atoms deposited on a terrace diffuse to the ascending step where they could nucleate and only a limited fraction of them nucleate on the terraces to form the islands. Examination of the various pictures of figure 1 does not permit to discriminate between the as-deposited and the annealed samples. This proves that, at the scale permitted with our STM pictures, no drastic rearrangement happen under mild heating conditions. Highest Pt coverages make the islands grow wider and wider. However no perfect Pt monolayer could be obtained as a second Pt layer starts growing beyond a deposited quantity in the 0.5 ML range. We refer to a previous paper [6] for a more detailed account of the STM observations on the as-deposited samples. It is worth noting now that LEED observations showed that the (1 x 1) picture was apparently unaffected by Pt deposition.

Using XPS the Pt 4f peaks were recorded before and after the annealing treatment. They could not be discriminated by a simple observation of the binding energy (71.05 eV for the Pt 4f_{7/2} peak) and intensity. However, the difference between the two spectra (annealed minus as-deposited) exhibit a faint residue shifted by 0.4 eV to high binding energies with respect to the peaks maxima. This could be compared with a Pt component located at 71.40 eV attributed to Pt diluted in the first layers of Co by Bulou et al. [10].

We now report the intensity change of the O 1s signal recorded by XPS after CO exposure versus the Pt coverage. We note that LEED observation of pure Co(0001) during CO exposure show the formation of a ($\sqrt{3} \times \sqrt{3}$) R 30° pattern superimposed to a ($\sqrt{7/3} \times \sqrt{7/3}$) R 10.9° pattern as already reported by various authors [11, 12]. These structures were attributed a CO coverage of 0.3 ML and 0.43 ML respectively. Our own calibration [9] gives 0.36 ML for the highest coverage we could obtain in this study. We think this is in perfect agreement with ref. [12] as the ($\sqrt{7/3} \times \sqrt{7/3}$)R10.9° pattern did not cover the entire surface area. The most striking feature appearing in the figure is the rapid decrease of the adsorbed CO coverage as soon as some Pt is deposited on the surface. Then, beyond a Pt coverage of 0.5 ML, the signal tends to stabilize around a mean CO coverage of 0.18 ML and 0.1 ML for the as-deposited and annealed data respectively. Moreover, this decrease is specially pronounced for the annealed samples. The simpler hypothesis to interpret this would be to consider that CO can only adsorb on the fractional area unoccupied by Pt on the surface. We have drawn on figure 2 (broken line) the evolution expected for the O 1s intensity under this assumption. The experimental data are clearly lower up to a Pt coverage of 0.5 ML. We already showed [9] that the Pt deposits actually

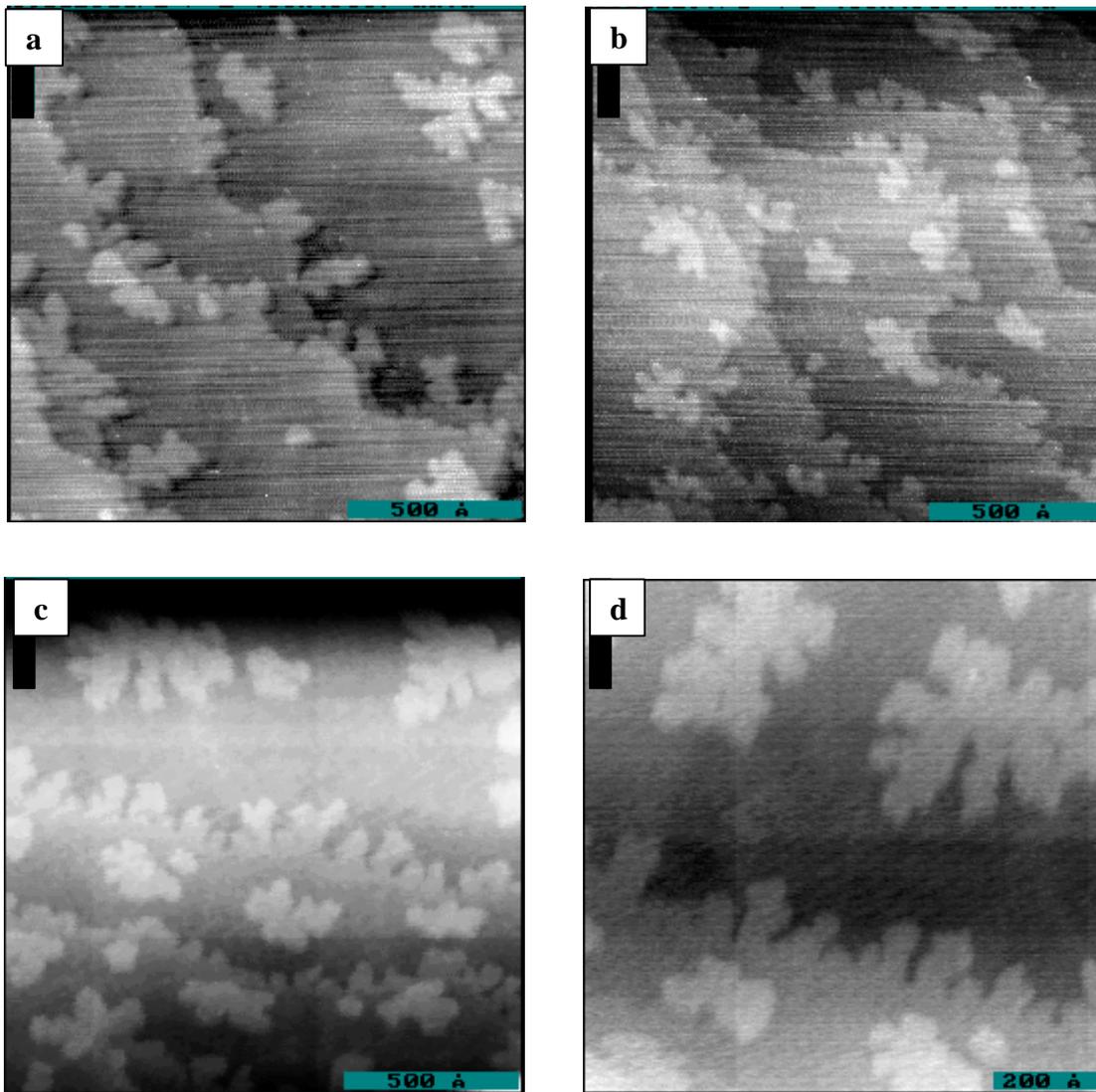


Figure 1. STM pictures of the Co(0001) surface after Pt deposition. a-b: as-deposited, $\theta(\text{Pt}) = 0.12$ ML, 150 nm x 150 nm; c: annealed sample, $\theta(\text{Pt}) = 0.18$ ML, 150 nm x 150 nm. d: annealed sample, $\theta(\text{Pt}) = 0.18$ ML, 100 nm x 100 nm.

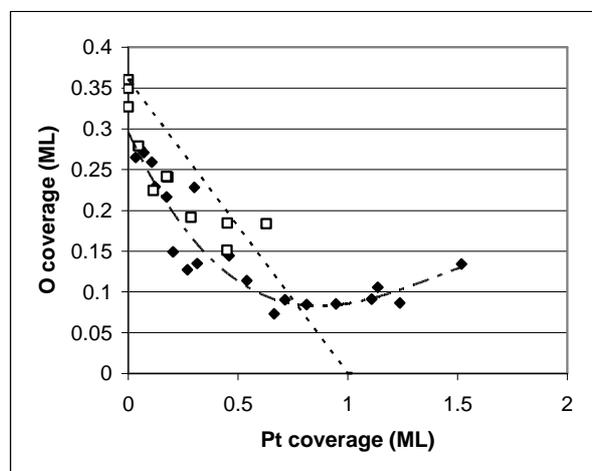


Figure 2. Evolution of the O 1s intensity after CO exposure versus Pt coverage. Empty squares: as-deposited Pt; Filled diamonds: annealed sample. The curve is a guide for the eyes. Broken line: see text.

adsorb CO although in lower quantity than the clean Pt(111) surface. Moreover, we proved that the adsorption energy of CO on Pt was decreased by some 40 % when Pt was supported by Co(0001). The conclusion we can extract from figure 2 is that the adsorbing power of the apparently free Co area observed by STM does also decrease. This could be understood recalling that Co is likely to be polluted by a limited quantity of Pt as concluded from XPS. We suggest that the Pt atoms diluted in Co, either in the surface plane or in the very sublayers, are responsible of the observed behavior. They could be already present as minute traces in the as-deposited surface. The thermal treatment certainly improves this tendency. We can consider as an example the case of an isolated Pt atom in the Co surface. It should induce a high compressive stress on its Co neighbors. Consequently their local electronic structure should be modified. It was shown that bond compression induces an upward shift of the d-band states resulting in a decrease of the CO adsorption energy [13]. By this way, one Pt atom could more or less induce passivation of 6 Co atoms.

Conclusion

We have showed that Pt submonolayer deposits on Co(0001) nucleate as one layer-thick dendritic islands on the Co terraces and stripes at the step edges. The STM observations do not permit to discriminate between the morphology of the as-deposited and the annealed Pt. However, the XPS data suggest a limited alloying of Pt in the first Co layers. This has dramatic consequences on the adsorptive power of both Pt and Co. On the Pt areas, the adsorption energy of CO was decreased by 40 %. Moreover, the Pt impurities passivate the apparently free Co areas.

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