Strain versus Substrate Interaction in Heteroepitaxial Metal Layers: Pt on Ru(0001)

A. Schlapka, M. Lischka, A. Groß, U. Käsberger and P. Jakob*

Physik-Department, Technische Universität München, 85747 Garching, Germany

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Abstract

By studying the adsorption of CO on up to 30 layers of Pt deposited on Ru(0001) the influence of surface strain on the adsorption energy has been disentangled from the residual chemical interaction with the substrate. While the electronic influence of the substrate has largely vanished for 3 Pt layers, the effect of surface strain due to the 2.5% lattice mismatch of Pt and Ru remains initially intact and is only gradually released for n $\geq$ 5 Pt layers. Electronic structure calculations confirm the experimental observations, in particular, the dramatic decrease of the CO adsorption energy on a single Pt layer which is caused by the strong Pt-Ru interlayer coupling. *Keywords:* Infrared absorption spectroscopy; Ruthenium; Platinum; Carbon monoxide; Low index single crystal surfaces

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* Corresponding author, email: peter.jakob@physik.uni-marburg.de, phone: +49-6421-28-24328, fax: +49-6421-28-24218

The effect of strain on the adsorption of chemisorbed particles on surfaces is of strong current interest since it might provide a means of manipulating adsorption properties quite significantly. In a recent experimental work, the preferential occupation of local areas with expanded lattices, as well as the depletion of compressed lattice areas has been demonstrated for oxygen adsorbed on Ru(0001) using scanning tunneling microscopy (STM) [1]. Theoretical studies confirmed these observations and suggested a general trend in the described way, based on a correlation of the d-band center with the adsorption energy: For transition metals with more than half-filled d-bands the energetic position of the d-band center shifts closer to the Fermi-level for expanded lattices (and reversely for compressed lattices) [2].

The application of external strain to modify the chemical properties of the substrate on a macroscopic scale is appealing. However, such an endeavor will prove ineffective, since metals easily form dislocations which release the strain. The anticipated lattice deformation therefore is limited to a few tenth of a percent which will hardly result in any significant modification of chemical activity. In the above mentioned experimental study [1] appreciable strain of the order of a few percent could be produced on a microscopic scale $(2 - 15$ nm$)$ only; Ar implantation due to Ar^+ ion bombardment and subsequent annealing caused accumulation of Ar to form subsurface cavities. These lead to a deformation of the surface, with expanded lattice areas on the top of protrusions and a compressed lattice zone at their rim.

A notable draw-back of the described experimental approach was the non-uniformity of the produced strain field; the associated difficulty to quantify the observed effects set serious limitations to the theoretical description. Improvements in this respect are highly desirable.

Heteroepitaxial (over)layers grown on a single crystal substrate represent a solution out of this dilemma. In favorable cases, the film grows pseudomorphically with a lattice constant identical to the substrate material; eventually, the film relaxes and continues growing with its own lattice parameters.

Besides adsorption energies, vibrational frequencies of probe molecules were also found to be influenced by lattice strain [3]. Quite often the influence of the substrate and of the lattice strain within the deposited layer produce a combined effect on the adsorption properties of chemisorbed species. Since both effects are usually observed simultaneously, it is difficult to uniquely separate their consequences. While the residual interaction of an adsorbate species with the underlying substrate will be substantial for a single layer, it is expected to gradually vanish for two, three or more layers. However, the exact range of

this interaction is not known. In addition, strain effects in many overlayer systems are also limited to a few layers before the strain is relieved by lattice dislocations.

For Pt/Ru(0001) bimetallic films it has now been possible for the first time to discriminate between the influence of lattice strain within a film and the residual interactions with the substrate on a macroscopic scale. Our combined experimental and theoretical study clearly demonstrates that the electronic influence of the substrate has largely vanished for more than 3 Pt layers while lattice strain remains fully operative up to at least n = 4 ML [4]. The films are very smooth up to coverages of 30 ML with step densities of only about 1% [5].

Infrared absorption spectroscopy (IRAS) and thermal desorption spectroscopy (TDS) were performed in a UHV chamber (base pressure 5×10^{-11} mbar) equipped with additional facilities for low energy electron diffraction (LEED) and x-ray photoemission spectroscopy (XPS). The Fourier transform IR spectrometer (Bruker IFS 66v) used in conjunction with a MCT detector is highly stable and evacuable. The Ru(0001) crystal could be cooled to 30 K and heated resistively to 1570 K by a computer controlled power supply. Pt was deposited by electron bombardment of a Pt rod (purity > 99.99%) using a commercial evaporator. The temperature range of Pt deposition and annealing was kept below 800 K to avoid intermixing at the Pt-Ru interface [6, 7]. The background pressure always stayed in the 10^{-11} mbar range during Pt evaporation.

To characterize the chemical properties of ultrathin Pt films on Ru(0001) we used CO as a probe molecule. Using infrared absorption the first, second and third Pt layers are well distinguishable. The thermal evolution of IRAS spectra in the spectral region of the internal CO stretch mode is plotted for two different Pt layers in Fig. 1 (Θ_{Pt} = 1.3 ML and 2.5 ML, deposited at 600 K). The spectra were taken after heating saturated layers of CO on Pt/Ru(0001) with 1 K/s to consecutively higher temperatures and recooling to 100 K. They clearly show a coverage dependent frequency shift from 2091 cm^{-1} (saturation coverage) to 2085 cm^{-1} (dilute layer) for CO on the first [8], from 2108 cm^{-1} to 2094 cm^{-1} for the second and from 2110 cm^{-1} to 2098 cm^{-1} for the third Pt layer on Ru(0001) [9]. The same procedure on the tenth (or 30th) Pt layer on Ru(0001) leads to an internal CO frequency at saturation coverage of 2108.5 cm^{-1} (2107 cm^{-1}) decreasing to 2093 cm^{-1} (2090.5 cm^{-1}) in the dilute limit. These latter numbers still differ from the respective values of CO on Pt(111) with 2105 cm^{-1} and 2089 cm^{-1} [10] (all numbers refer to a temperature of 100 K).

The surface morphologies at 4 ML and 8 ML Pt on Ru(0001) are displayed in Fig. 2,

along with line scans as indicated in the images. For both layers smooth Pt films with terrace widths similar to the underlying Ru(0001) substrate are found. At 8 ML (Fig. 2B) we clearly identify a large scale dislocation network as deduced from the quasi-periodic depressions (their origin most likely is due to a combined geometric and electronic effect [11]). We note that the film is not yet fully relaxed at this layer thickness; according to the separation of the dislocations ($\Delta l \approx 250$ Å) we conclude that lattice strain due to the 2.5 % lattice mismatch is released only by 40 %. This value agrees well with the evolution of adsorption energies of a probe molecule (CO) for n $\geq$ 4 ML (see Fig. 3). The 4 ML Pt film (Fig. 2A), on the other hand, is completely free of dislocations or other types of surface modification which could be associated with strain relaxation (e.g. island formation). Atomically resolved images confirm the hexagonal structure of the bimetallic surface. We conclude that Pt grows pseudomorphically on Ru(0001) up to at least 4 ML and, for higher film thicknesses, gradually releases strain within the film by forming large scale dislocation networks.

A key parameter describing the adsorptive and chemical properties of strained transition metals is the binding energy of a probe particle such as CO. From the IR measurements shown in Fig. 1 and from additional thermal desorption spectra the desorption temperature of small amounts of CO on the various Pt/Ru(0001) layers were determined. In the dilute limit the desorption temperature is a suitable measure for the binding energy since the interaction between adjacent adsorbate particles is negligible. The results are summarized in Fig. 3A; as a reference, the desorption temperature of CO on Pt(111) is indicated by a dashed line. In each case desorption from defects (steps) is easily identified and disregarded in the analysis. For CO on the first Pt layer on Ru(0001) the desorption temperature, T_{des}, is dramatically reduced from $450 - 460$ K on Pt(111) to 320 K (see also [6]). For an increasing number of Pt layers, T_{des} rises until, approximately at the fourth layer, it seems to converge at about 430 K, which is still significantly below the value for CO on Pt(111). In order to obtain a reference value for the Pt(111) surface, 30 layers of Pt have been deposited which gave a desorption temperature of 455 K (heating rate of 3 K/s). As $T_{\mathrm{des}}(24 \text{ layers}) = T_{\mathrm{des}}(30 \text{ layers}) - 1.3$ K, we conclude that the value at 30 layers pretty much represents a Pt(111) crystal.

In Fig. 3A we clearly distinguish two regimes: For $n = 1 - 3$, a rapid increase of the CO bond strength is observed, while for $n \geq 4$ the CO binding energy E_B changes only slowly

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with Pt layer thickness. In fact a slight increase is found for thicker Pt layers which can be traced to the beginning of strain relaxation within the Pt film as some dislocations were observed for n = 8 ML in STM (Fig. 2). Up to n = 4 ML the film remained perfectly flat and retains its hexagonal structure as confirmed by atomically resolved STM.

Assuming a pre-factor for desorption of $k_0 = 10^{15}$ s^{-1} which seems a reasonable value for on-top bonded CO on a transition metal surface [12], CO binding energies of 0.99 eV (1st layer), 1.21 eV (2nd layer) and about $1.30 - 1.35$ eV for higher layers are derived.

To further support our analysis and to deepen our understanding of the adsorbate-substrate interaction, first principles density-functional theory (DFT) calculations with the generalized gradient approximation (GGA) of Perdew *et al.* [13] were performed using the Vienna *ab initio* simulation package (VASP) [14, 15]. The projector augmented wave (PAW) method [16, 17] was used to accurately describe the CO bonding situation. The surface was modeled by a four layer thick Ru(0001) substrate slab with one to five overlayers of laterally compressed Pt in a $p(2 \times 2)$ surface unit cell. The in-plane Pt-Pt nearest neighbor distance was set to the theoretical Ru equilibrium value of 2.73 Å. For reference purposes, CO binding energies were also computed on an unstrained four layer Pt(111) slab with its computed nearest neighbor distance of 2.82 Å and on a four layer Pt slab compressed by 3.2% to match the theoretical Ru lattice constant of 2.73 Å. The latter slab thus served as a model for an infinitely thick stack of laterally compressed Pt overlayers, especially as adsorption energies change by less than 3 meV when doubling the number of layers to 8. In all calculations, the two bottom Ru or Pt layers were kept fixed at their truncated bulk positions whereas all other layers were relaxed such that the forces on each atom were below 0.02 eV/Å. An energy cut-off of 400 eV and a $4 \times 4 \times 1$ **k** point grid proved sufficient to obtain converged total energies.

In order to avoid any errors induced by the GGA due to a different chemical bonding situation [18] the CO molecule was fixed to the on-top position, in accordance with IRAS - data. The change of the adsorption energies as a function of the number of deposited Pt layers are thus reliable. The obtained on-top binding energies of CO on nPt/Ru(0001) for a $p(2 \times 2)$ overlayer (coverage $\theta_{CO} = 0.25$ ML) are shown in Fig. 3B. As already seen in the experiments, the effects of the Ru(0001) substrate and the compression of the Pt layers are clearly separable: Within the accuracy of our DFT calculations, adsorption energies have converged to the value obtained on a strained pure Pt slab starting with the third Pt layer

on Ru(0001). Adsorption energies of CO on 1Pt/Ru(0001) and, to a somewhat lower extent, 2Pt/Ru(0001) are found to be clearly lower compared to compressed Pt(111), due to the presence of the underlying Ru(0001) substrate.

According to our calculations the isolated effect on CO adsorption energies of just compressing the Pt(111) surface by 3.2% amounts to $0.20 - 0.25$ eV; this value is significantly larger than the energy change reported for CO on a compressed Ru(0001) surface [2] (about 0.02 eV for 1.5% compression), but quite close to the value reported for PtCo surface alloys [19]. In particular for thin Pt layers the influence of the substrate is of equal importance and, for a single Pt layer, clearly exceeds the strain effect. However, as outlined above, the electronic influence of the underlying substrate decays rapidly with layer thickness and is not noticeable for $n \geq 4$.

The fact that a single Pt layer is significantly less reactive with respect to CO adsorption (binding energy reduced by 0.33 eV) can be attributed to the strong inter-layer bonding between the first Pt layer and the Ru substrate. This also manifests itself in a strong downshift of the d states of the surface Pt atoms. According to the Hammer-Nørskov model [20–22], the CO binding energy should be proportional to the center of the locally projected d-band of the surface atom. As shown in Fig. 4 there is indeed a strong correlation between the d-band center, ε_d, and the binding energies, E_B, for Pt layers of variable thickness on Ru(0001).

The experimentally observed pure strain effect on E_B seems to be slightly less in comparison to the theoretical results (Fig. 3). This could be attributed to dissimilar coverages used in the experiment (dilute layer) and in the theoretical calculation ($p(2 \times 2)$ supercell). There are indeed subtle coverage effects as can be seen from the calculated adsorption energies of a $(\sqrt{3} \times \sqrt{3})$R30° CO overlayer ($\theta_{\mathrm{CO}} = 0.33$ ML) included in Fig. 3B. Furthermore, the equilibrium lattice constants of Pt and Ru computed within DFT overestimate the experimentally observed lattice mismatch by about 25%. This might also slightly distort the reported values. Considering these facts, the agreement is very good.

In conclusion, we have disentangled the two major, intrinsic effects affecting the chemical properties of heteroepitaxial metal layers, i.e. lattice strain within the grown film and the residual electronic influence of the substrate, by a combination of experimental and theoretical methods. Layer dependent studies of the adsorption energy and vibrational frequency of a probe molecule (CO) show that the electronic influence of the substrate dominates for thin

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films $(1-3$ layers) whereas strain related effects remain active for thicker pseudomorphic overlayers. Both, the lattice compression of the Pt overlayers as well as the strong Pt-Ru interlayer coupling lead to a significant reduction of the CO adsorption energy which can be understood in terms of the d-band center downshift caused by both effects.

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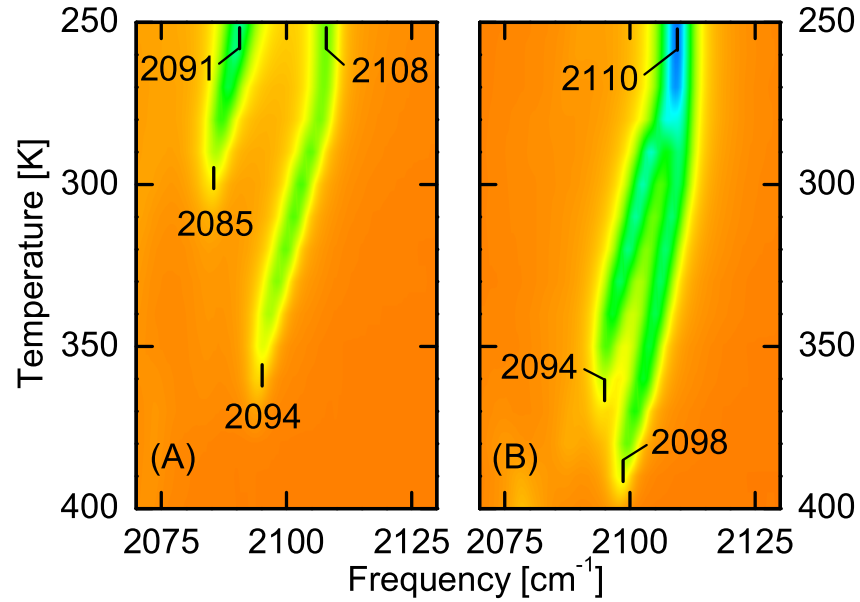[22] B. Hammer, O. H. Nielsen, and J. K. Nørskov, Catal. Lett. **46**, 31 (1997).

Figures

FIG. 1: (online color) Pseudo-3d plot of IR spectra obtained after heating saturated CO layers on Pt/Ru(0001) films (adsorbed at 80 K) to the indicated temperatures (ordinate) and recooling to 100 K. In panel (A) 1.3 ML Pt have been deposited; in panel (B) this value has been increased to 2.5 ML. The observed frequency shifts are attributed to thermal desorption of CO. The color is indicating the reflectivity change from 0% (red) to 10% (blue) with the edges of the peaks clearly visible as yellow (or light gray, respectively) contours.
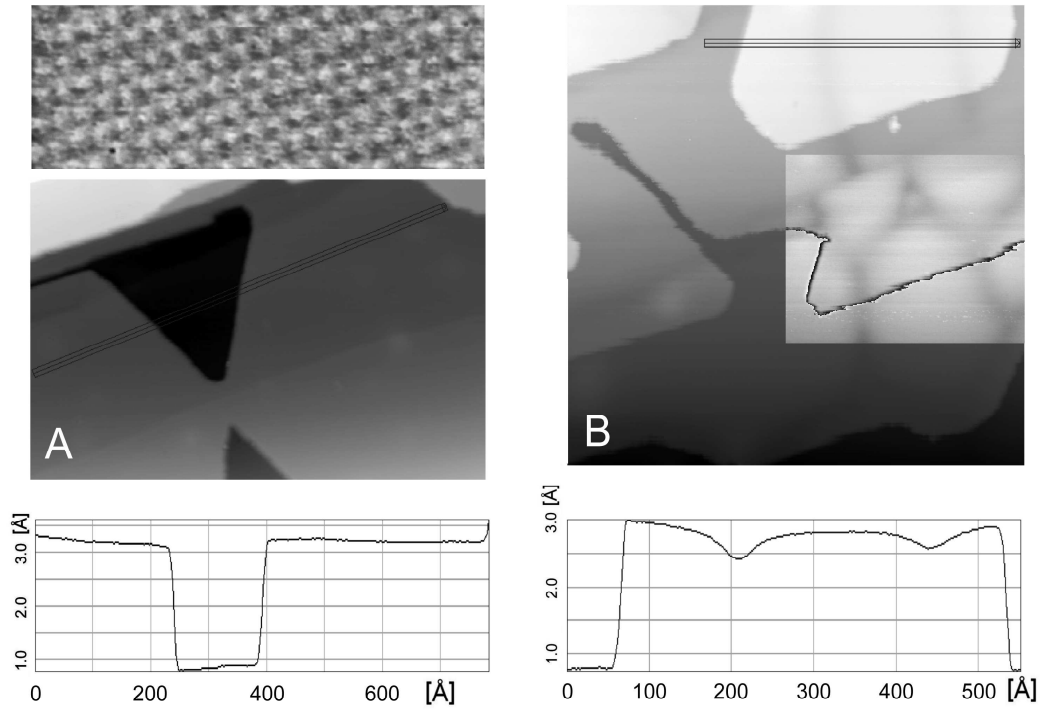
FIG. 2: STM images of bimetallic Pt/Ru(0001) layers grown at $T_G = 600$ K at a rate R $= 5 \times 10^{-4}$ ML/s. (A) Topography (800 Å $\times$ 530 Å) and line scan (l $= 780$ Å) of a 4 ML Pt film; also shown is an enlarged area (50 Å$\times$ 17 Å) displaying the hexagonal lattice of the pseudomorphic Pt layers. (B) Topography (800 Å$\times$ 800 Å) and line scan (l $= 550$ Å) of a 8 ML Pt film. Apparently, dislocation lines are formed for 8 ML Pt films while they are absent at 4 ML. The grey scale within the rectangular area (420 Å$\times$ 330 Å) has been adjusted to improve the visibility of the dislocations.

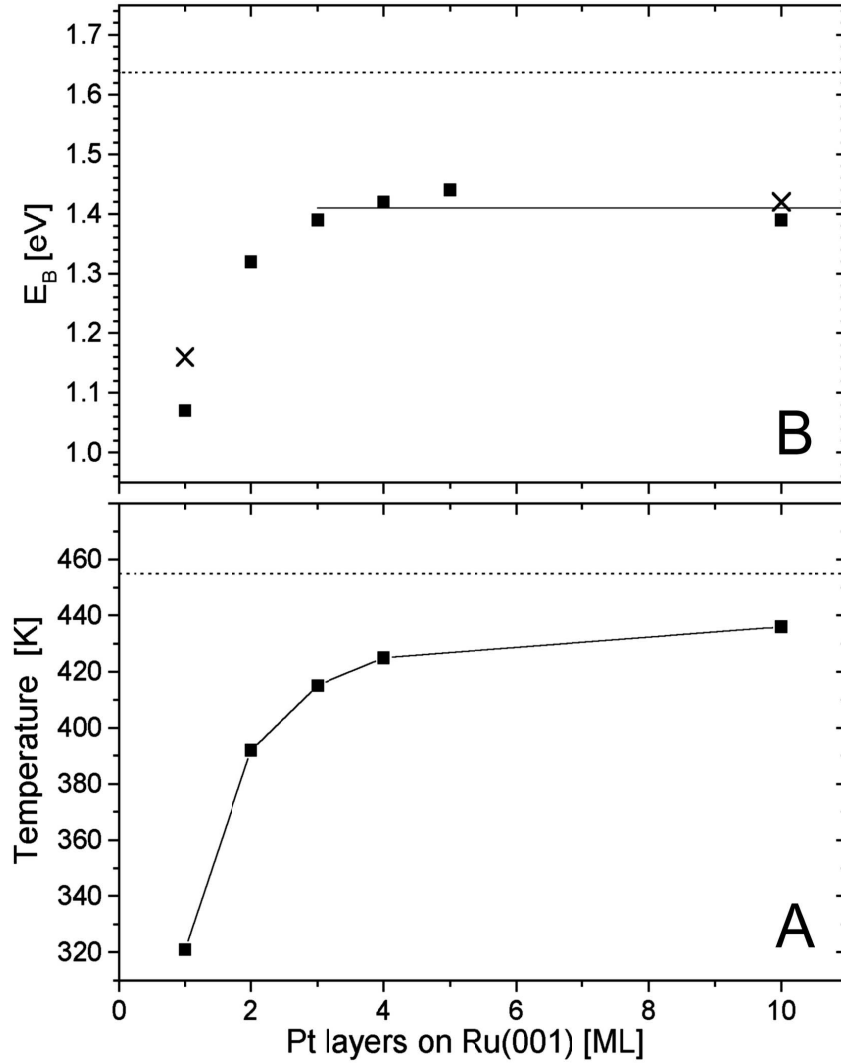FIG. 3: (A) Desorption temperatures of CO from nPt/Ru(0001) layers (trailing edge of a TD spectrum taken from a high coverage layer) from IR spectroscopy and TDS. The dashed line indicates the desorption temperature of small amounts of CO from the terraces of a Pt(111) surface at a heating rate of 3 K/s. (B) On-top CO binding energies on nPt/Ru(0001), for strained Pt (Ru lattice constant) for a $p(2 \times 2)$-CO (solid box) and a $(\sqrt{3} \times \sqrt{3})$R30° CO overlayer ($\times$). The solid line marks the average binding energy for $n \geq 3$. For comparison, the calculated binding energy of CO on unstrained Pt(111) is indicated by the dashed line. Note that the slight increase in the CO desorption temperature for n$\geq$ 4 in (A) is due to the onset of strain relaxation within the film which is not considered in the theory.
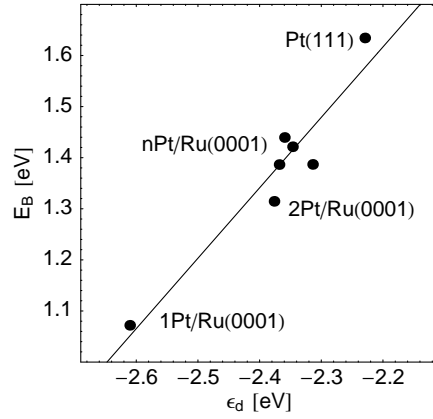
FIG. 4: CO binding energy, E_B, for a $p(2 \times 2) - CO$ ordered overlayer versus d-band center, ε_d, (with respect to the Fermi energy) of the surface Pt atom. The solid line represents the best least-squares linear fit.