Surface stress effects in chemical activation

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Abstract

The adsorption of CO on Cu covered Pd(110) has been studied using reflection absorption infrared spectroscopy and scanning tunneling microscopy. In the submonolayer Cu coverage range the presence of Cu islands induces on uncovered Pd(110) terraces a CO configuration change. This intriguing effect is not localized at Cu island boundaries (steps) but is of mesoscopic character penetrating up to 40 Å onto uncovered Pd terraces. Potential origins of the substrate modification are discussed. Most likely the mesoscopic CO configuration change is caused by the buildup of stress in the Pd substrate due to the substantially strained Cu islands.

1. Introduction

Since the discovery by Döbereiner [1] that chemical reactions may be catalyzed by the interaction with the surface of a metal, scientists have been fascinated by the magic of heterogeneous catalysis. Undoubtedly, the surface science approach, i.e. studying chemical reactions at clean surfaces of single crystals under carefully controlled conditions, has promoted substantially our understanding of catalytic processes [2]. A central concept evolving out of these studies is that of 'active' sites [3,4]. In this picture structural imperfections such as steps and kinks act as local highly reactive sites promoting the surface reaction.

The idea of local active sites has also been transposed to reactions on more complex multicomponent surfaces. A particularly promising class of multicomponent catalysts are bimetallic surfaces, which are found to have superior chemical activity and/or selectivity compared to their single metal counterparts [5]. The origin of this enhanced activity is not understood well but generally discussed in terms of

ensemble or ligand effects, both of which are local reaction scenarios [6,7]. The geometric ensemble effect is based on the idea that a given reaction needs a minimum number of adjacent atoms of the active metal. The electronic ligand effect, on the other hand, relates to a local electronic modification of the active metal component in the close neighborhood of the inactive metal deposit.

In this Letter, we show that long-range interactions due to surface stress may play a crucial role in the chemical activation at bimetallic surfaces. These interactions are the natural consequence of the structural misfit between the lattice parameter of the substrate and the adlayer. According to the long-range character of elastic forces the chemical properties of the surface are modified on a mesoscopic length scale rather than on a local atomic scale. Surface stress has been found to be responsible for a number of other mesoscopic surface phenomena, including surface reconstruction [8], domain ordering [9] and pattern formation during surface alloying [10] and surface oxidation [11].

A surface stress induced chemical modification is

proposed here for CO adsorption on Cu/Pd(110). This system has been studied because CuPd catalysts have shown an enhanced reactivity for CO oxidation compared to pure Cu and Pd [12]. In the submonolayer Cu coverage range the presence of Cu islands induces on uncovered Pd(110) terraces a change in adsorption configuration. These results have been obtained from a synergic scanning tunneling microscopy (STM) and a reflection absorption infrared spectroscopy (RAIRS) study. This combination offers a unique possibility of correlating a surface chemical analysis with atomic-level surface structure.

2. Experimental

STM and RAIRS are combined together in a UHV system with a base pressure of 1×10^{-10} mbar, described in detail in Ref. [13]. The Pd(110) surface is unreconstructed [14], and consists of close packed atom rows running in the [1$\bar{1}$0] direction separated by a distance of 3.89 Å, corresponding to the Pd lattice parameter. The crystal was prepared by repeated cycles of ion sputtering at 700 K and annealing at 950 K. This procedure resulted in a sharp LEED pattern with low diffuse background. Cleanliness of the surface and deposited Cu films was routinely verified by Auger electron spectroscopy (detection limit < 1%) and STM directly. The sample exhibited an average terrace width of about 85 Å; however, terraces up to a width of 2000 Å were observed occasionally. The high step density is not due to a miscut of the sample (nominally 0.2°), since up- and down-steps are present to the same extent. It can rather be associated to a checkerboard-type terracing of the surface attributed to the low step free energy for Pd(110) and/or the presence of tensile stress [15,16]. Copper (purity 99.99%) was evaporated from a Knudsen cell at a fixed rate of 10^{-3} monolayers per second (1 ML = 9.35×10^{14} atoms/cm^2) at the indicated substrate temperatures. All STM measurements were performed in the constant current mode at 0.2–1 V positive or negative tip bias and 0.5–1.5 nA tunneling current. No influence of the tunneling parameters on the apparent surface morphology was observed. The RAIRS spectra were recorded at 4 cm^{-1} resolution with 500 scans accumulated; all spectra shown have been corrected for the baseline.

3. Results

The infrared spectrum of CO adsorbed on clean Pd(110) at $T_S = 150$ K (saturation coverage) is shown in Fig. 1, characterized by a sharp absorption peak at 2007 cm^{-1}. Simultaneously, a (2×1)p1g1 LEED pattern is observed. This structure was initially interpreted as being CO molecules sitting in twofold bridge sites and tilting alternately to the side in order to minimize steric repulsions [17,18]. A second minority state can be populated upon direct exposure of the crystal to 10^{-7} mbar CO at low temperatures, giving rise to an additional higher frequency band at 2095 cm^{-1} (see inlay in Fig. 1, $T_S = 140$ K). This was attributed to a fast compression due to the adlayer immobility at low temperatures which results in the formation of small (2×1)p1g1 islands with top-bound CO molecules at the domain boundaries, showing an absorption at 2095 cm^{-1} [17,18].

The frequency of the dominant band at 2007 cm^{-1} lies in the gray area midway between typical values for bridge and top bonded species. Indeed, a structural analysis using TLEED [19] re-assigned the 2007 cm^{-1} band to the top site, the CO molecule being tilted by 11° with respect to the surface normal. In this picture the identification of the 2095 cm^{-1} band becomes difficult, since all absorption frequencies higher than 2007 cm^{-1} must likewise be assigned to top species. In this context it is
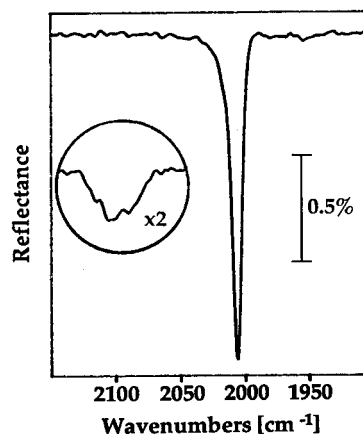

Fig. 1. Infrared spectrum of CO adsorbed on Pd(110) at $T_S = 150$ K (saturation coverage). Inset: second absorption band populated upon exposure to the crystal at 10^{-7} mbar CO at 140 K.

interesting to compare the behaviour of CO on different low-index Pd surfaces. On Pd(100), CO forms with increasing coverage a series of $(n \sqrt{2} \times 2)R45°$ structures ($n = 2, 3, 4$) with the molecules adsorbed on bridge sites [20], showing an infrared absorption peak at $1997 \, cm^{-1}$ at saturation ($T_S = 80 \, K$) [21]. As on Pd(110), a second higher-frequency peak can be populated under special conditions [22]. On Pd(111) three absorption bands develop depending on CO coverage and temperature, at 1895, 1962 and $2110 \, cm^{-1}$, indicating the subsequent population of threefold hollow, twofold bridge and top sites [23,24]. CO absorption on thin Pd films deposited on metallic substrates results in high frequency ($> 2070 \, cm^{-1}$) absorption bands attributed to top sites [25,26]. Keeping in mind this situation, we will further refer to the $2007 \, cm^{-1}$ CO absorption band on Pd(110) as the 'a-species' and to the $2095 \, cm^{-1}$ band as the 'b-species'.

The growth of copper on Pd(110) has been studied in the temperature range $150 \leqslant T_S \leqslant 600 \, K$ [27]. At submonolayer coverages, the surface morphology of the system is substantially determined by the anisotropy of Cu diffusion, reflecting the symmetry of the Pd substrate unit cell. The energy barriers of diffusion have been determined to be $E_{\langle 1\bar{1}0 \rangle} = 0.51 \, eV$ and $E_{\langle 001 \rangle} = 0.75 \, eV$ [28]. The large difference between these barriers leads to the formation of Cu islands with large aspect ratios. At 300 K, migration across the close packed Pd rows, i.e. along [001] is nearly frozen in. Thus at low Cu coverages ($\Theta_{Cu} \leqslant 0.1 \, ML$), long linear Cu chains oriented along [1$\bar{1}$0], monatomic in width, are present on the surface [28]. At intermediate coverage ($\Theta_{Cu} = 0.35 \, ML$, Fig. 2), the average width of an island is about 20 Å, corresponding to about six atoms, but the length reaches more than 1000 Å. The islands are locked into a (1×1) structure on the Pd(110) surface, as revealed by LEED.

In the multilayer range, Cu grows three-dimensionally to about 350 K. Fig. 3 (left side) displays a series of STM images showing the growth of Cu at $T_S = 400 \, K$. On smaller terraces, Cu nucleates at step edges. Islands are formed only on larger terraces, the islands still being elongated along the [1$\bar{1}$0] direction of the substrate. Thicker copper layers grow at this temperature in a Stranski–Krastanov mode with a critical thickness of one monolayer, i.e. multilayer
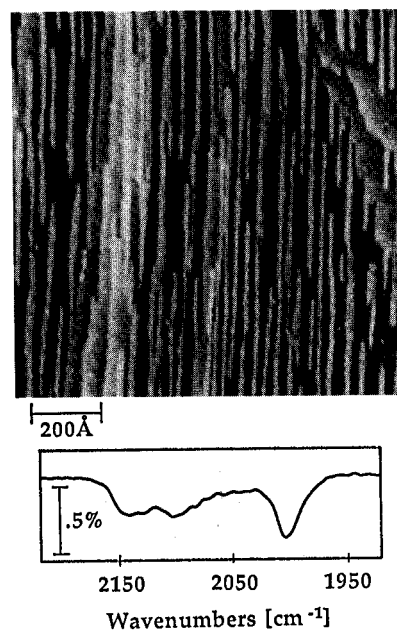

Fig. 2. STM image of 0.35 ML Cu on Pd(110) deposited at $T_S = 300 \, K$ (image size $1200 \, Å \times 1200 \, Å$). Infrared spectrum of CO adsorbed at $T_S = 150 \, K$ on this surface.

Cu films consist of large three-dimensional clusters located on top of the pseudomorphic first Cu layer, their edges being accurately oriented along the preferential directions of the substrate. Increasing the deposition temperature to $T_S = 600 \, K$, a transition to a layerwise growth in a pure step flow mode occurs, persisting up to $\Theta_{Cu} = 10 \, ML$. Above this critical coverage, three-dimensional growth sets in.

On the right-hand side of Fig. 3 we have plotted the infrared spectra of CO adsorbed onto Cu/Pd(110) surfaces as a function of Cu coverage. Cu was previously deposited at 400 K. 10 L of CO were dosed onto the surface at 150 K to ensure saturation coverage. Annealing to 200 K before recording the IR spectra was performed to allow ordering of the CO layer. The IR spectrum of CO on clean Pd(110) is also displayed for reference. A copper coverage of $\Theta_{Cu} = 0.15$ induces a new broad CO absorption feature around $2100 \, cm^{-1}$. With increasing copper coverage it develops into two distinct bands at $2147 \, cm^{-1}$ (fwhm $25 \, cm^{-1}$) and $2019 \, cm^{-1}$ (fwhm $32 \, cm^{-1}$). The high-frequency band has maximum intensity at $\Theta_{Cu} = 1.05$, where its peak maximum has shifted down to $2136 \, cm^{-1}$ and its linewidth is reduced to $15 \, cm^{-1}$.
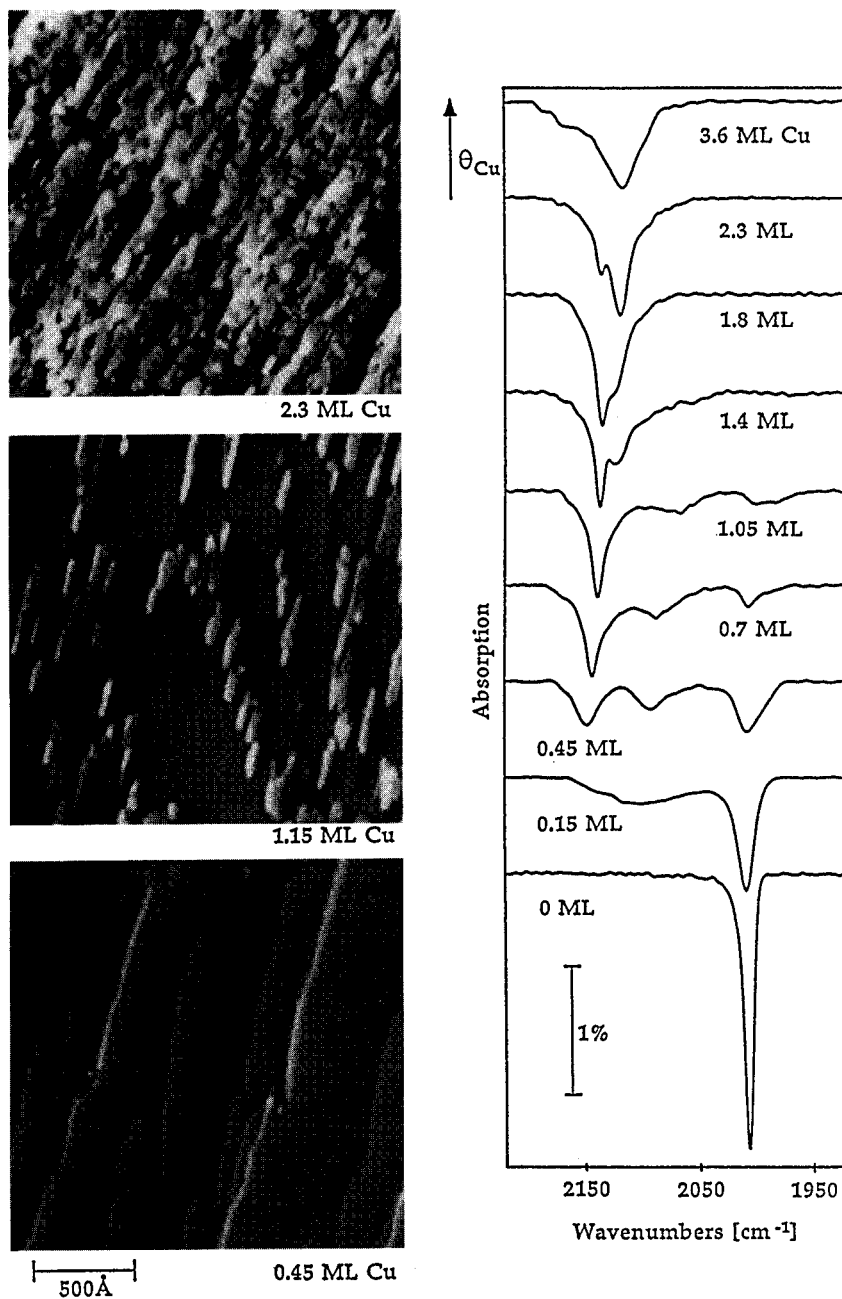
Fig. 3. Left side: STM images showing the growth of Cu on Pd(110) at $T_s=400$ K. All images span 2000 Å×2000 Å. Right side: infrared spectra of CO on Cu/Pd(110) surfaces with increasing Cu coverage. Cu was deposited at $T_s=400$ K before dosing the surface to CO at $T_s=150$ K.

The two lower-frequency bands at 2091 and 2007 cm^{-1} decrease continuously in intensity as well as in frequency and disappear slightly above $\Theta_{Cu}=1$.

In the multilayer range the absorption band at 2136 cm^{-1} loses intensity without further frequency shift, whereas a new feature appears at 2120 cm^{-1}

(fwhm 25 cm^{-1}), being dominant above $\Theta_{Cu}=2$. At higher Cu coverages ($\Theta_{Cu}=3.6$), a broad band at 2110 cm^{-1} remains. Its frequency shifts slowly downwards and finally resembles the spectrum of CO on a polycrystalline Cu film [29].

4. Discussion

By comparing STM and RAIRS data the assignment of the different CO absorption bands can be done straightforwardly. The two high-frequency bands, being the only ones present in the multilayer regime, correspond to CO molecules adsorbed on copper sites. Fig. 3 suggests that CO adsorbed on the three-dimensional Cu clusters gives rise to the peak at 2120 cm^{-1} whereas the band at 2136 cm^{-1} is associated with CO bound on top of Cu atoms in the first flat layer. This frequency is unusually high for the CO/Cu species. We relate this phenomenon to the strain in the first Cu layer, growing pseudomorphically on the Pd substrate. The Pd lattice constant is 7% higher than the Cu bulk value; the electron density in the first Cu layer is thus considerably lower in comparison to the (110) face of bulk Cu. As a consequence the amount of backdonation of electrons into the antibonding $2\pi^*$ orbital of CO being responsible for the decrease in the C–O stretch frequency upon adsorption on a metal surface, is reduced. It can even be shown that the C–O stretch frequency depends linearly on the strain in a Cu film, which can be tailored by deposition of Cu on substrates with different lattice mismatch [30].

The occurrence of the strong absorption band at 2091–2070 cm^{-1} is surprising. This band could probably also be assigned to CO on Cu sites, but its disappearance at Cu coverages above $\Theta_{Cu}=1$ indicates that this band is due to CO on Pd substrate sites. Its frequency coincides with that of the b-species on clean palladium but its population is dramatically increased in the presence of Cu islands. Two observations confirm the assignment of the absorption peak at 2091–2070 cm^{-1} to the b-species of CO on Pd(110). Firstly, Fig. 4a shows the vibrational spectra of CO adsorbed on Cu/Pd(110) at $\Theta_{Cu}=0.45$ as a function of increasing CO coverage. The different Pd substrate sites are first populated whereas CO adsorbs on Cu sites only after higher exposure. The fre-
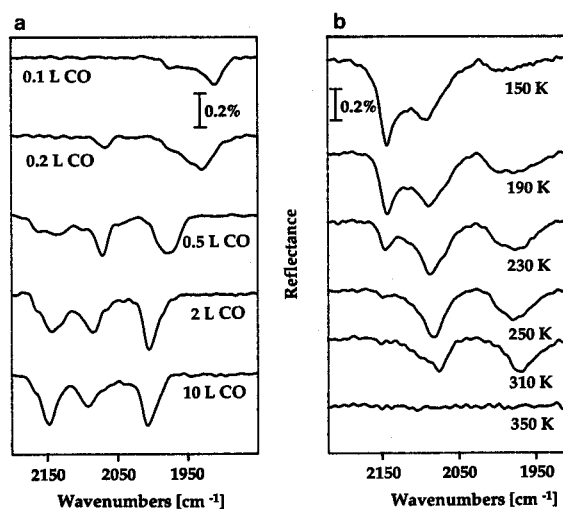

Fig. 4. (a) Infrared spectra of CO on Cu/Pd(110) as a function of CO exposure ($\Theta_{Cu}=0.45$ deposited at $T_s=400$ K, CO adsorbed at $T_s=150$ K). (b) Infrared spectra of CO adsorbed at 150 K (saturation coverage) on 0.6 ML Cu deposited at 400 K on Pd(110) and after annealing the CO layer to the indicated temperatures.

quency behaviour of the band arising from the a-species (<2000 cm^{-1}) is complex [18] and will not be discussed here. The peak maximum of the absorption band assigned to CO molecules bound to Cu exhibits only a small (2 cm^{-1}) coverage induced shift. This behaviour is typical of CO/Cu systems [31]. By contrast, the band assigned to CO bound to Pd sites undergoes a strong (28 cm^{-1}) upward frequency shift, which is characteristic of CO adsorption on transition metals. Secondly, upon annealing we observe the desorption of CO on Cu sites at 230 K, whereas the two lower-frequency bands assigned to CO on Pd sites both disappear only upon annealing at 350 K (Fig. 4b).

Coadsorbate-induced site changes of CO in themselves are not too surprising and have been observed in a number of systems including coadsorption with benzene [32] or alkalis [33]. In these cases the adsorption site change is localized, only affecting CO molecules neighboring the coadsorbed species. Such locally induced site changes have also been observed in the bimetallic system Cu/Ni(111) [34]. Under certain conditions, only Ni top-site CO is observed instead of Ni–CO bridge species, being thermodynamically favored on Ni(111). This is attributed to 2D mixing of Ni and Cu, generating isolated Ni

atoms. The concomitant observation of a mixed CuNi bridge site strongly supports this assumption.

Although a mixed CuPd site is not populated in our case, it is worthwhile to discuss the possibility that the 2091–2070 cm^{-1} band arises from CO molecules adsorbed on isolated Pd atoms in a Cu matrix generated by a mixing process, the band frequency being only accidentally similar to the b-species on the clean surface. Such an assignment would imply a monolayer confined alloying of the bimetallic system having a maximum miscibility around half-monolayer coverage followed by demixing upon increasing coverage, a phenomenon which has been observed for Cu growth on W(100) [35] and Ag growth on Pt(111) [36] at elevated temperatures. Indeed we have shown that Cu adatom diffusion along the [001] direction (across the close packed Pd atom rows) is mediated by a CuPd exchange process [28]. This process becomes increasingly probable with increasing Cu deposition temperature and thus we would expect an increase in the 2091 cm^{-1} band intensity. However, the exact opposite is observed. While at a Cu coverage of 0.45 ML grown at 300 K about 50% of the total amount of CO molecules populates Pd b-sites, this percentage *decreases* to 35% for Cu growth at 400 K and to 30% for Cu deposition at 600 K.

Indeed, from the measured barriers for Cu adatom diffusion we can estimate that the amount of Pd incorporated in the Cu island is low in the deposition range of concern here. At 300 K (Fig. 2), the ratio of Cu adatom jumps along [1$\bar{1}$0] and exchange processes along [001] is about 20000; the creation of isolated Pd adatoms is, therefore, a rare event. We have additionally shown by calculations using the embedded atom method that for thermodynamic reasons, an isolated Pd adatom will be incorporated back into the first Pd substrate layer by a second CuPd exchange, ensuring phase separation during the whole growth process [28]. Finally we note that upon annealing or direct growth above 700 K alloying via the diffusion of Cu into the Pd substrate indeed occurs, indicated by clear changes in the corresponding CO infrared spectra.

From the discussion above we conclude that CuPd intermixing in the submonolayer regime is unlikely to be responsible for the appearance of the band at 2091 cm^{-1}. This band must be attributed to the population of the b-species on uncovered Pd substrate terraces. An explanation for the increase in occupation of the Pd b-species which suggests itself upon inspection of Fig. 2 is the local configuration change at Cu island edges. The picture of steps as local active sites can easily be examined by studying the CO adsorption on a copper submonolayer deposited at lower temperatures. At 300 K the nucleation density of Cu islands is 8.5 times higher than at 400 K (see Fig. 2). In addition the aspect ratio of the condensed Cu islands is 3 times larger at 300 K [28], in total giving rise to a Cu island step length increased 13 times at identical coverage (this is even an underestimated value since at 300 K additional islands are formed on narrower terraces). Fig. 2 shows the corresponding CO infrared spectrum for $\Theta_{Cu} = 0.35$. Although the total Cu step length is increased by more than one order of magnitude, the total amount of CO in the Pd b-geometry has increased by only 15%, as revealed by a comparison of the peak intensities at the two temperatures and identical coverages.

Even a simple look at the amount of configuration-converted CO demonstrates that a local scenario cannot be appropriate: at 400 K (300 K) and a Cu coverage of $\Theta_{Cu} = 0.45$ about 35% (50%) of the total amount of adsorbed CO occupy Pd b-sites. These numbers do indeed speak in favor of a *long-range modification* of the Pd substrate by the adsorbed Cu islands. Two phenomena may cause such mesoscopic modifications: modified electronic density of states or stress effects due to the lattice mismatch between Cu and Pd.

The Cu island edges act as barriers to electron waves. The interference between incident electron waves and waves reflected from a step edge results in the formation of standing waves and the modulation of the electronic density of states near the step. These two-dimensional electron standing waves have been measured directly in two STM experiments [37,38]. The electron density modulations are indeed found to have mesoscopic decay-lengths up to 100 Å. In this picture the total amount of site-converted CO should also scale with the total Cu step length reflecting the electron waves, which is, however, not seen in the experiment (see above). The STM experiments showed in addition that the change in potential at the step leads preferentially to electron reflection at the upper terraces, which in our case are the Cu islands or Cu terraces. We can thus conclude that electronic long-

range modifications are unlikely to be the cause of the observed adsorbate site change.

Long-range elastic interactions, on the other hand, offer a natural explanation for the altered chemical properties of the Pd(110) terraces. As already mentioned, because of the large mismatch (7%) between the Cu and Pd lattice parameters the adsorbed Cu islands are substantially strained with respect to bulk Cu. The strained islands exert a force on the substrate which induces a build up of stress in the topmost Pd layers. The observation of a long-range ordering of the Cu islands at intermediate coverages is a direct indication of the presence of such stress [27]. In Fig. 2, for instance, the islands are not distributed homogeneously along the [001] direction. The probability of measuring island–island separations of 40, 80 and 120 Å, corresponding to nearest, second and third neighbour island distances, is significantly enhanced. Such a quasi-periodic island ordering on a mesoscopic scale can indeed be attributed to the presence of surface stress [39]. The stress induced in the substrate by the strained Cu islands is supposed to decay logarithmically with the distance from the island center and its amplitude should scale with the mass of the adlayer island [40]. It is the latter fact which explains the small difference of CO in the population of Pd b-sites on the Cu/Pd(110) surface with the Cu islands grown at 300 and 400 K. While at 300 K ($\Theta_{Cu} = 0.35$) the total island boundary is about 13 times larger the mass of an average island is 8.5 times smaller than at 400 K.

To gain more insight into the stress induced modification of the Pd(110) surface a detailed analysis of the 600 K case is particularly useful. At this temperature the first Cu layer wets the substrate in a pure step flow mode. The corresponding CO infrared spectra (not shown) exhibit three bands, similarly to the spectra obtained upon Cu deposition at 400 K. The band assigned to CO on Cu sites increases monotonically in intensity whereas the band corresponding to the Pd a-species decreases and disappears at $\Theta_{Cu} = 1$. The intensity of the absorption peak of CO on Pd b-sites reaches a plateau between $\Theta_{Cu} = 0.4$ and $\Theta_{Cu} = 0.5$, decreasing in intensity at higher Cu coverages. The behaviour of the band intensities of CO on Pd sites rules out the possibility that sharp domain boundaries exist between CO on a- and b-sites. Otherwise, a-site CO would not be observable at high Cu

coverages and the decrease of the b-site would start later. More likely, the amount of CO adsorbed on Pd b-sites increases monotonically towards a Cu step edge, in coexistence with CO on Pd a-sites. From the behaviour of the 2095 cm^{-1} band it can be concluded that a low Θ_{Cu}, the penetration of the Cu island induced substrate stress increases almost linearly with Θ_{Cu} until a saturation value at $\Theta_{Cu} = 0.4$ is reached. The onset of the intensity decrease of the 2095 cm^{-1} peak at $\Theta_{Cu} = 0.5$ leads to an estimation of the penetration depth of the substrate modification of 40 Å or about 10 Pd atomic spacings, keeping in mind the average terrace width of only 85 Å.

In summary, we emphasize that the deposition of heteroepitaxial metal layers can influence the chemical properties of the substrate modifying them on a mesoscopic length scale. These modifications are likely to be due to buildup of surface stress in the substrate. This effect may be of importance for other bimetallic surfaces with significant structural misfit.

Acknowledgement

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