Correlation between Surface Stress and the Vibrational Shift of CO Chemisorbed on Cu Surfaces

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We demonstrate a correlation between the frequency of the ν(CO) stretch vibration of chemisorbed CO and the surface stress of Cu substrates. The surface stress is tailored by pseudomorphic growth of Cu multilayers on mismatched single crystal substrates. The CO stretch frequency is found to vary linearly with the inherent copper strain. An intuitive model to explain this intriguing relation is proposed.

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The observation of the vibrational spectra of adsorbed molecules provides one of the most powerful methods for understanding surface chemical processes. The analysis of the internal vibrational modes of a chemisorbed species not only identifies its chemical nature ("fingerprint") but also reveals details about the bonding configuration at the surface and its local environment [1].

When a CO molecule adsorbs on a metal surface the frequency of the ν(CO) stretch vibration decreases from its gas phase value (2143 cm^{-1}) by about 50–200 cm^{-1}. This vibrational shift has several origins, but in general is dominated by the chemical bonding configuration at the surface [2]. It is this "site specificity," which allows us to discriminate between adsorption in on-top, bridge, or hollow configuration and hence is at the origin of the popularity of surface vibrational spectroscopy of adsorbed molecules [3].

Besides the dominating shift due to the chemical bonding at the surface there are additional vibrational shifts caused by the local chemical environment and the surface morphology which the adsorbing molecule is experiencing. The influence of lateral chemical interactions on vibrational frequencies and intensities has largely been explored and our understanding has approached an advanced level [4]. The origin of the frequency shift related to the surface morphology, however, is not evident. While the decrease in frequency for a CO molecule bound at defect sites, like steps, can easily be interpreted in terms of higher coordination, the variation in frequency for identically bound CO molecules on different low-index crystal surfaces of the same metal is far from being understood.

An ideal model system to explore the physical origin of the structural frequency shift is the chemisorption of carbon monoxide on copper. On all low-index single crystal surfaces of this metal CO is found to be adsorbed in an on-top configuration [5–7]. The measured ν(CO) stretch frequency increases from 2070 through 2087 to 2094 cm^{-1}, for the (111) [5], (100) [6], and (110) surface [7], respectively (the frequency varies only slightly with coverage [7]; the values listed are for CO saturation coverage at temperatures between 80 and 140 K). This trend is suggestive of a decisive influence of the surface tension on the vibrational shift: The vibrational frequency of chemisorbed CO increases with decreasing surface atomic density, i.e., with increasing surface tension.

In the present Letter we prove the existence of a correlation between the surface stress of Cu substrates and the vibrational shift of chemisorbed CO. Low-index Cu surfaces of varying stress have been tailored by growing flat pseudomorphic Cu multilayers on mismatched transition metal surfaces. The vibrational shift of the CO is found to scale linearly with the copper strain. For Cu films under tensile strain the frequency of the CO stretch increases with respect to the corresponding unstrained Cu surface, while for Cu films under compressive strain the frequency decreases.

Experiments have been done in an UHV system combining reflection absorption infrared spectroscopy (RAIRS) and scanning tunneling microscopy (STM) besides conventional surface preparation and analysis facilities; a detailed description of the setup is given in Ref. [8]. Cu films on Pd(110) and Pd(100) are grown by vapor phase epitaxy applying a commercial Knudsen cell at a fixed rate of about 10^{-3} monolayers (ML) per second. All STM measurements were performed in the constant current mode at 0.2–1.0 V positive or negative tip bias and 0.5–1.5 nA tunneling current. CO chemisorption on the Cu multilayers was investigated by RAIRS. The infrared spectra were recorded at 4 cm^{-1} resolution with 500 scans accumulated; all spectra shown have been corrected for the baseline.

In the thermodynamic limit the growth mode of a thin film is determined by the surface free energies of film and substrate and the interface energies between successive layers [9]. Depending on their value the system achieves the lowest total energy either by growing layer by layer (Frank–van der Merwe growth, FM), three dimensional (Vollmer-Weber growth, VW), or by a transition from the first to the latter growth mode upon reaching a critical film thickness (Stranski-Krastanov growth, SK). Kinetic limitations can, however, drive a system, which in the thermodynamic limit would grow smoothly, towards rough interfacial growth. The decisive process that determines in the kinetic regime the actual growth mode is the interlayer mass transport [10] which can be controlled through the choice of deposition temperature and deposition flux.

The tailoring of the Cu-film growth mode on Pd(110)

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through control of the deposition temperature is demonstrated on the right-hand side of Fig. 1. The STM series nicely reflects the transition from VW growth at 300 K to FM growth at 600 K with an intermediate regime of SK growth around 400 K. At 300 K the Cu grows three dimensionally above deposition of about 0.7 ML. The Cu clusters nucleating in the higher layers are very small in size (10–30 Å) leading to a large microroughness. In the SK growth regime the first monolayer is completed before 3D growth sets in; islands nucleating in the second and third layers still have appreciable size (50–300 Å). At 600 K the Cu multilayers are found to grow layer by layer up to at least 12 layers. Up to a thickness of 5 ML the Cu films are pseudomorphic, as evidenced by the sharp (1×1) low energy electron diffraction (LEED) pattern *and* the flat imaging by STM. In particular, the absence of any misfit dislocation lines in the STM images prove the perfect pseudomorphic (1×1) structure of the film [11]. Between 6 and 12 ML the strain of the film is partially reduced by a uniaxial compression of 3.4% along the [110] direction; the thick Cu multilayers are commensurate with the substrate with a $[29 \times 1]$ unit cell [12]. Up to temperatures of 700 K the Cu layers grow completely phase separated on Pd(110).

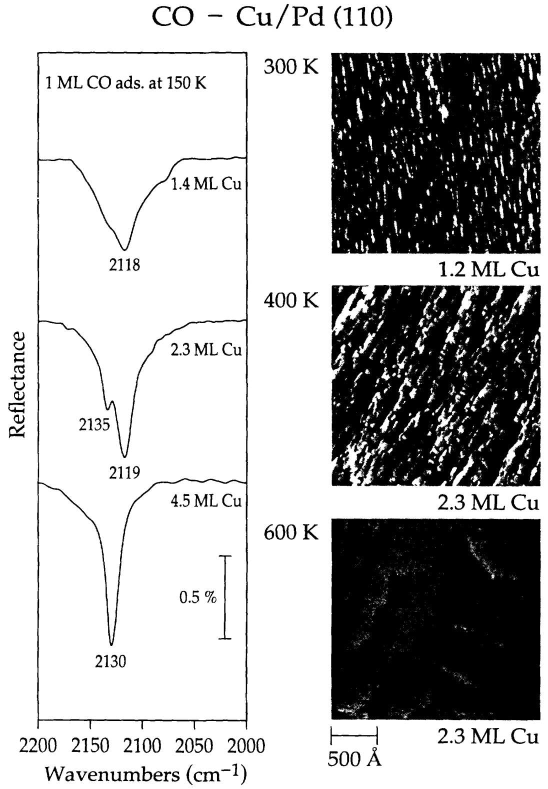

FIG. 1. Right-hand side: STM images characterizing the growth morphology of Cu multilayers on Pd(110) as a function of deposition temperature. Left-hand side: morphology dependence of the infrared spectra of CO chemisorbed on Cu/Pd(110).

The chemisorption of CO on the different Cu films is characterized by RAIRS spectra shown on the left-hand side of Fig. 1. After deposition of the Cu film at the indicated temperature the sample was cooled to 150 K and an infrared background spectrum was recorded. Subsequently the crystal was heated to 250 K and exposed to 10^{-7} mbar CO upon recooling to 150 K, at which temperature the CO RAIRS spectrum was recorded. The analysis of the CO-IR spectra versus CO dose reveals that CO saturation is reached for all Cu films studied here between 6 and 8 L (1 L= 10^{-6} Torr s). The total CO exposure in Figs. 1–3 was 10 L, ensuring saturation coverage. The observed CO infrared spectra nicely reflect the film morphology.

The VW growth of Cu at 300 K is characterized by the presence of one broad (40 cm^{-1} FWHM) absorption band centered around 2118 cm^{-1}, which is assigned to CO molecules linearly adsorbed on small three-dimensional Cu clusters. The RAIRS spectrum at 300 K Cu deposition resembles very much that taken from polycrystalline Cu films or high-indexed (highly stepped) Cu crystal surfaces [13].

In the SK growth regime (400 K) the Cu multilayer is characterized by two CO frequencies at 2119 and 2135 cm^{-1} (Θ_{Cu} = 2.3 ML), both characteristic for on-top configuration. The comparison with the corresponding STM image suggests that CO adsorbed on the three-dimensional Cu clusters gives rise to the band at 2119 cm^{-1}, whereas the peak at 2135 cm^{-1} can be associated with CO bound to Cu atoms in the first flat layer. LEED measurements reveal that the CO molecules on the first flat Cu monolayer form an ordered (2×1) structure, giving rise to the sharp feature at 2135 cm^{-1} (the same superstructure is found for CO chemisorption on the flat multilayers grown at 600 K; see below).

The flat pseudomorphic Cu multilayer (Θ_{Cu} = 4.5 ML) grown at 600 K is characterized by the presence of one sharp IR band at 2130 cm^{-1}. This peak is narrowest at monolayer Cu coverage (10 cm^{-1}); it broadens slightly and shifts to lower frequencies with increasing Cu layer thickness. The frequency shift of the flat Cu multilayers on Pd(110) as a function of layer thickness is shown in Fig. 2. The ν(CO) stretch frequency only slightly decreases with increasing Cu thickness; for the 10 ML thick Cu film the frequency is still blueshifted by as much as 30 cm^{-1} with respect to the Cu(110) surface.

At first glance this result is surprising. Whereas a relation between adlayer-substrate coupling and the metal-CO bond strength is well established [14], the C-O stretch frequency variation upon "transfer" from one surface to another surface is much more difficult to interpret since many parameters affecting the C-O stretch frequency are changed simultaneously. In general, the frequency shift due to electronic adlayer-substrate coupling is expected to decay rapidly with increasing thickness of the adlayer. Thus the C-O stretch frequency should reach the CO/Cu(110) frequency (2094 cm^{-1}) with increasing

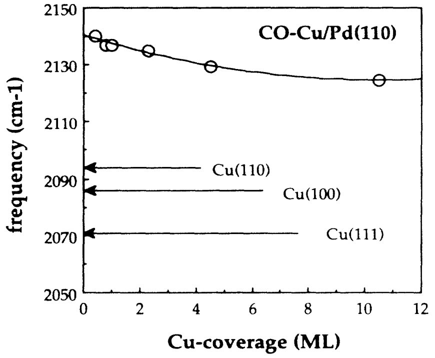

FIG. 2. Frequency of the ν(CO) stretch on pseudomorphic Cu multilayers grown at 600 K on Pd(110). Also indicated are the frequencies of CO saturation layers adsorbed on the low-index surfaces of bulk copper.

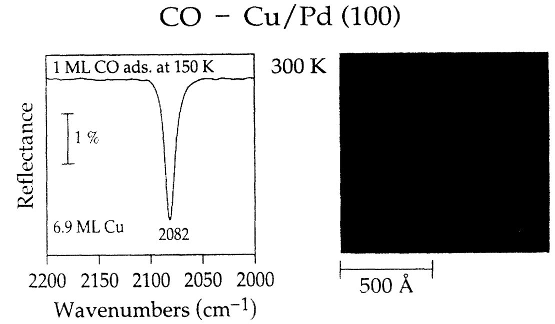

FIG. 3. Right-hand side: STM image characterizing the growth morphology of bct-Cu on Pd(100) at 300 K. Left-hand side: infrared spectrum of CO chemisorbed on the bct-Cu film (6.9 ML) grown at 300 K on Pd(100).

film thickness. Since the large blueshift (58 cm^{-1}) of the ν(CO) stretch for the Cu monolayer, which would indicate a substantial modification of the Cu electronic properties through the Pd substrate, is only marginally reduced with increasing Cu film thickness, electronic adlayer-substrate coupling is inappropriate as an explanation for this shift.

The high CO-Cu/Pd(110) frequency and its small decrease with increasing film thickness can, however, be understood straightforwardly in a picture relating the vibrational frequency of chemisorbed CO to the surface stress of the substrate. The Cu multilayers grow pseudomorphic on the Pd(110) substrate. They are thus under substantial tensile stress due to the Cu(fcc)-Pd(fcc) strain which amounts to $(d_{\mathrm{Pd}}^2 - d_{\mathrm{Cu}}^2)/d_{\mathrm{Cu}}^2 = 0.154$ for the pseudomorphic (1×1) multilayers ($\Theta_{\mathrm{Cu}} \leq 5$ ML) and remains still at 11.6% for the thicker (29×1) commensurate multilayers ($\Theta_{\mathrm{Cu}} > 5$ ML). According to the general trend on Cu surfaces—increasing frequency with increasing surface tension—this tensile strain should increase the CO stretch frequency with respect to the "strain free" Cu(110) surface.

To corroborate this interpretation further we have studied the CO chemisorption on Cu/Pd(100). The electronic adlayer-substrate coupling is expected to be similar to that for the Cu/Pd(110) system, while the tensile stress of the Cu multilayers is substantially smaller. The reduced stress in this system relates to the fact that Cu multilayers on the Pd(100) substrate grow in a novel bct-Cu phase [15,16]. The in-plane copper nearest neighbor distance in bct-copper is increased to 2.76 Å. Accordingly the strain in bct-Cu/Pd(100) films is substantially reduced and changes sign, i.e., is weakly compressive, $(d_{\mathrm{Pd}}^2 - d_{\mathrm{Cu\text{-}bct}}^2)/d_{\mathrm{Cu\text{-}bct}}^2 = -0.0073$. In Fig. 3 we summarize the RAIRS and STM results for pseudomorphic Cu multilayer films on Pd(100). From the STM and LEED measurements we deduce a layer-by-layer growth of the pseudomorphic bct-Cu phase at 300 K up to about 7 ML. The corresponding RAIRS spectrum for a CO saturation layer reveals a sharp absorption band decreasing from 2096 cm^{-1} for a copper monolayer down to 2082 cm^{-1} for a 7 ML thick copper film. The thick Cu film under weak compressive stress is hence characterized by a small negative CO frequency shift with respect to CO/Cu(100) (2087 cm^{-1}).

Both the much smaller initial blueshift for the Cu monolayer [9 cm^{-1} with respect to CO/Cu(100)] and the small redshift for the thick Cu film (due to the compressive nature of the strain) strongly support our interpretation of CO frequency shifts in terms of surface stress.

The direct relation between the surface stress of Cu substrates and the CO stretch frequency is proven in Fig. 4. Here we have plotted the vibrational shift of the CO stretch (normalized to the frequency on the corresponding bulk Cu surface) on pseudomorphic Cu multilayers as a function of the copper surface strain. Besides the two systems studied in this Letter we have included data from pseudomorphic (1×1) Cu multilayers grown on Pt(111) [17], Rh(100) [18], and Ni(111) [19]. The data points have been calculated with the ν(CO) frequency measured for

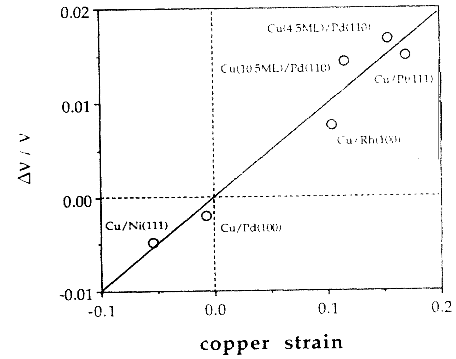

FIG. 4. Vibrational shift of the ν(CO) stretch frequency (normalized to the frequency of the corresponding bulk Cu surface), $(\nu_{\mathrm{Cu\text{-}film}} - \nu_{\mathrm{Cu\text{-}crystal}})/\nu_{\mathrm{Cu\text{-}crystal}}$, for pseudomorphic Cu multilayer films as a function of copper strain $(d_{\mathrm{Cu\text{-}film}} - d_{\mathrm{Cu\text{-}bulk}}^2)/d_{\mathrm{Cu\text{-}bulk}}^2$.

the thickest pseudomorphic Cu films studied in order to minimize contributions from the adlayer-substrate electronic coupling; Pd(110): 10.5 ML Cu; Pd(110): 4.5 ML Cu; Pd(100): 6.9 ML Cu; Pt(111): 2.6 ML Cu; Rh(100): 2 ML Cu; and Ni(111): 8 ML Cu. The experimental data cover strained copper layers from compressive strains of -5.4% up to tensile strains of $+15.4\%$. The result of Fig. 4 is self-explanatory: The vibrational shift scales linearly with the copper strain. For Cu multilayer films under tensile strain the frequency of the CO stretch increases with respect to the corresponding unstrained Cu surface, while for Cu films under compressive strain the frequency decreases.

Details of the Cu/Pt(111) data [17] give additional support for this intriguing relation between surface stress and ν(CO) stretch frequency. In the experiment of Rodriguez *et al.* the pseudomorphic (1×1) Cu film on Pt(111) was produced by evaporation of 2.6 ML Cu at 80 K and successive annealing to 250 K. The CO stretch frequency for chemisorption on this highly strained Cu film was measured to be 2101 cm^{-1}, which is the data point shown in Fig. 4. Annealing of the Cu film above 400 K, however, results in a breakdown of the pseudomorphic structure producing a nearly stress free film with Cu(111) terraces. In the experiment this strain relief was indeed found to be accompanied by a dramatic frequency decrease to 2081 cm^{-1}, close to the CO/Cu(111) value.

A plausible conception to account for the intriguing relation between surface stress and ν(CO) stretch frequency is the intuitive "pillow model." The chemisorption bond of CO on a Cu surface is governed by the positive σ contribution due to the metal $4sp\sigma$-CO 5σ interaction and a negative contribution arising from the transfer of electron density from the metal into the empty 2π orbitals of the CO molecule and by the polarization of its molecular orbitals through charge localized at the metal center. *Ab initio* calculations by Müller and Bagus [20] for Cu_nCO clusters demonstrate that the effect of the π donation is dominant. This π back donation into the antibonding molecular orbitals weakens the C-O bond and leads to a decrease of the ν(CO) stretch frequency [21]. Because of the "pillow effect," the available electron density for back donation of a strained Cu surface is a linear function of the strain. In a strained pseudomorphic layer the atom density is different from the corresponding bulk plane. If the film atom density is lower (tensile strain) the electron density also decreases and thus the total charge density which is available for π back donation is smaller; hence the C-O bond is stiffened and the frequency increases. In the inverse situation of higher atom density in the film plane (compressive strain) the electron density increases and the ν(CO) stretch frequency decreases due to the enhanced π back bonding.

The variation of the surface charge density with the atom density is consistent with recent observations in surface phonon spectroscopy of Cu surfaces using thermal energy He atom scattering. In these experiments anomalously large intensities of longitudinal surface phonon resonances were observed [22]. This result was rather surprising, as thermal He scattering is mainly sensitive to charge density modulations perpendicular to the surface. In the pillow model the enhancement of the longitudinal phonon resonances is easy to understand: Longitudinal motion of surface atoms increases or decreases locally the electron density, building up a substantial perpendicular corrugation which is detected by the thermal He atoms [23].

In conclusion, we have demonstrated a correlation between the surface stress of Cu substrates and the ν(CO) stretch frequency of linearly bound CO. This intriguing relation can be explained with an intuitive model which accounts for the variation of the total surface charge density with the atom density in the surface plane.

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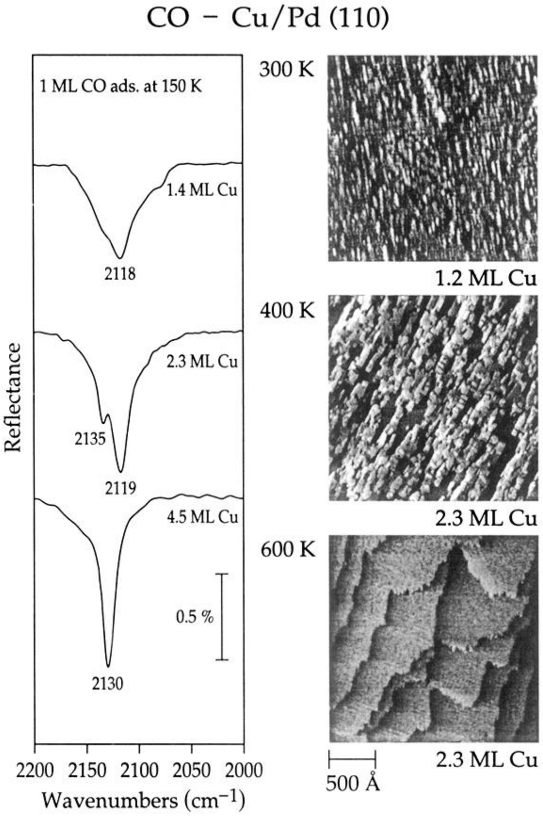

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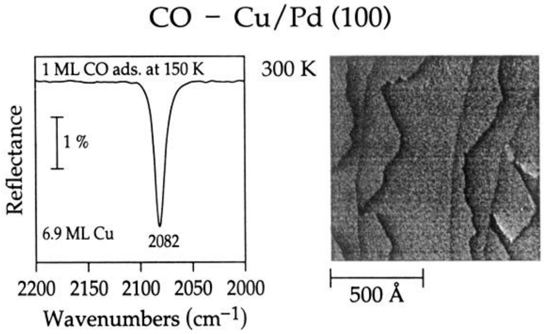

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