An AES, LEED, and CO chemisorption study of copper overlayers on Rh(100)

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A model bimetallic system Cu/Rh(100) has been prepared by the thermal evaporation of copper onto a Rh(100) surface and studied by Auger electron spectroscopy, low-energy electron diffraction, and CO chemisorption. At 115 K, the copper overlayer growth follows a layer-by-layer mechanism at least to the third layer. The first monolayer grows pseudorandomly with respect to the Rh(100) substrate while the second monolayer grows epitaxially with a Cu(100) structure. Upon annealing the copper film, the first two layers are stable up to the copper desorption temperature while the copper deposits in excess of two layers nucleate to form three-dimensional copper islands on top of the copper bilayer. For CO chemisorption, copper blocks rhodium sites on a one-to-one basis and induces a weakening of the Rh–CO bond. CO on monolayer copper on Rh(100) exhibits an enhanced bonding strength with respect to bulk copper. The CO chemisorptive properties are discussed in the context of the electronic and geometric structures of this model bimetallic system.

1. Introduction

Bimetallic systems have been the subject of intensive research because of their importance in a variety of catalytic technologies [1,2]. Oftentimes mixed-metal systems have structural, electronic, and chemical properties quite different from those of either component, and frequently exhibit superior catalytic activity, selectivity, and stability [1,2].

The adsorption of CO on copper and on rhodium are examples of weak and strong chemisorption systems, respectively. A goal of the present study is a better understanding of the effects of copper and rhodium on each other in the mixed Cu/Rh system with respect to CO chemisorption. From a practical point of view, the Cu/Rh system is important potentially with regards to the methanol synthesis reaction from CO and H₂. Both copper and rhodium effectively catalyze this reaction [3–5]. In fact, copper is a major constituent in many highly active methanol synthesis catalysts. Whether Cu(I) cations or metallic copper centers comprise the active site(s) is still a subject of intense debate [6–8].

CO adsorption on Rh(100) [9,10] and bulk copper [11,12] has been investigated by several groups. It has been found that CO chemisorbs on Rh(100) and forms well-ordered surface structures at a substrate temperature < 300 K. At low coverage, CO forms a c(2 x 2) structure. With increased CO exposures, the c(2 x 2) structure is compressed into a close-packed overlayer. CO desorbs molecularly from Rh(100) with a desorption peak maximum at ~ 500 K. A low temperature shoulder appears concomitantly with the onset of compression of the CO overlayer. On Cu(100) and Cu(111), CO forms several ordered structures at low adsorption temperatures (~ 80 K). The first to appear on Cu(100) is a c(2 x 2) structure, and on Cu(111), a (\sqrt{3} x \sqrt{3})-30° structure. Further adsorption leads to essentially close-packed structures.

CO chemisorption on a variety of model bimetallic systems has been studied in which one metal is evaporated onto a second single-crystal...
metal surface [13–28]. It has been demonstrated for many bimetallic systems, e.g., Cu/W(110) [18], Cu/Ru(0001) [19], Pd/Cu(100) [20], Ni/W(110) [23], Pd/W(110) [24], and Ni/Ru(0001) [26], that CO adsorbs associatively and desorbs molecularly from the metal overlayer at a temperature distinctly different from that of the bulk metal. A recent XPS study [29] has shown that the perturbation of the CO desorption temperature correlates very closely with the shift in the surface core level binding energy of the overlayer metal. That is, a reduction in the binding energy of the surface core level of the overlayer is accompanied by an enhancement in the strength of the bond between CO and the metal overlayer. This increase in the metal–CO bond-strength, in turn, leads to an increase in the CO peak desorption temperature. An opposite result for the CO chemisorptive properties is seen for an increase in the overlayer core binding energy.

The CO/Cu/Rh(111) system has been investigated by Foord and Jones [17] who showed that growth of (111) oriented copper films takes place via a three-dimensional (Volmer–Weber) growth mechanism. Island coalescence was found to occur at a total copper coverage of around two monolayers. Also copper was shown to efficiently block the strong chemisorption of CO on Rh(111), whereas the Rh–CO bond was found to weaken in the presence of copper. The experiments of Foord and Jones [17] were carried out at 300 K thus no CO adsorption on the copper overlayer was observed.

In this paper, we report the results of a study of copper overlayer growth on Rh(100) and CO chemisorption on this model bimetallic system studied by Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and thermal desorption spectroscopy (TDS).

2. Experimental

The experiments in this study were performed in an ultrahigh vacuum chamber described in detail previously [30]. It is equipped with a double pass cylindrical mirror analyzer with an integral electron gun for Auger electron spectroscopy, LEED optics for low-energy electron diffraction observation, and a quadrupole mass spectrometer for thermal desorption measurements. This chamber is pumped by a titanium sublimation pump and an ion pump; the base pressure is in the low $10^{-10}$ Torr range.

The high-purity Rh(100) single crystal was polished using a series of emery papers and diamond paste until a mirror finish was obtained. High purity tantalum wires (0.020 inch diameter) connected to feedthroughs immersed in a liquid nitrogen reservoir were spot-welded to the periphery of the crystal to provide resistive heating and conductive cooling. A pair of W–5%Re/W–26%Re thermocouple wires spot-welded to the edge of the crystal were used to monitor the temperature of the crystal.

Research-grade oxygen and carbon monoxide, supplied by Matheson Gas Products, Inc., were used.

The crystal cleaning procedure consisted of oxidation in $1 \times 10^{-7}$ Torr oxygen at 1150 K for 10 min and annealing at 1200 K for 5 min. A capillary doser in front of the crystal was used to direct the oxygen and CO to the crystal surface so that the local pressure near the crystal during oxidation and CO adsorption was much higher than the background pressure. CO exposures were carried out at a substrate temperature of 115 K.

Copper was evaporated onto the Rh(100) single-crystal surface at a substrate temperature of 115 K by resistively heating a tantalum wire wrapped with high purity copper. Following evaporation, the sample was annealed to 750 K and cooled to 115 K prior to CO adsorption, unless otherwise stated.

A linear heating rate of 10 K/s was used in all the desorption experiments.

3. Results

3.1. Copper deposition

Although the Cu–Rh system can exist both as a solid solution and as an alloy [31], it is very unlikely that these form under the present experimental conditions. Indeed, recent XPS results show
no apparent change in the Cu(2p\textsubscript{3/2}) or Rh(3d\textsubscript{5/2}) binding energies following deposition of Cu onto Rh(100) at 100 K with subsequent anneals up to 900 K [29]. After repeated desorption experiments of copper, the AES of the rhodium sample did not exhibit a detectable copper signal. Clearly, if stable Cu–Rh solid solutions or alloys form, their concentrations are below the AES detection limit.

The thermal desorption spectra of copper from Rh(100) at various coverages are shown in fig. 1. At low coverages, copper desorbs from a single state (\(\beta\)) centered at 1255 K, with the peak maximum temperature remaining nearly constant with increasing copper coverage. The temperature required to reach a fixed desorption rate (indicated by the hatch marks on the lowest three traces in fig. 1) shifts to a lower value as the copper coverage increases. At higher copper coverages, a second desorption peak (\(\alpha\)) develops at a lower temperature, with little change in the overall shape and intensity of the \(\beta\) state. The peak maximum of the \(\alpha\) state shifts to a higher temperature with increasing copper coverage and the traces exhibit a common leading edge. These characteristics suggest that desorption from the \(\alpha\) state is zero order whereas desorption from the \(\beta\) state is first order.

The \(\beta\) desorption state corresponds to copper in direct contact with the rhodium while the \(\alpha\) state is attributed to desorption of copper multilayers. Using the Redhead algorithm [32] and assuming a pre-exponential factor of \(10^{13} \text{ s}^{-1}\), the activation energy of desorption for the \(\beta\) state is estimated to be 327 kJ mol\(^{-1}\). This value is greater than the sublimation energy of bulk copper (317 kJ mol\(^{-1}\) [33]), indicating a stronger interaction between copper and rhodium than between copper atoms. Leading edge analysis of the \(\alpha\) state gives an activation energy comparable to that of bulk copper sublimation.

Fig. 2 shows a plot of the Cu(60 eV)/Rh(302 eV) Auger peak intensity ratio versus copper TDS area. The plot consists of three linear segments, indicating that the copper overlayer growth follows the Frank–van der Merwe, i.e., layer-by-layer, mechanism at least to the third layer, with each break corresponding to the completion of one monolayer (ML). In fact, point “a” in fig. 2 correlates with the onset of copper desorption from peak “\(\alpha\)” in fig. 1. It can be seen from fig. 2 that the first and second monolayers have different TDS areas, indicating that they have different copper atomic densities. The ratio of the first to the second monolayer TDS areas, 0.95, compares favorably with the ratio of the surface atomic densities of Rh(100) and Cu(100), 0.91, using the values \(1.38 \times 10^{15}\) and \(1.53 \times 10^{15}\) cm\(^{-2}\) for the atomic densities of Rh(100) and Cu(100), respectively.

Fig. 3 shows the Auger peak intensity ratio as a function of the crystal anneal temperature for different copper coverages, \(\theta_{\text{Cu}}\). For \(\theta_{\text{Cu}} \leq 2\) ML, upon annealing, the Auger intensity ratio increases initially and reaches a maximum at 500–700 K, indicating a higher degree of order and the elimination of defects in the copper overlayer. For \(\theta_{\text{Cu}} \leq 1\) ML, the Auger intensity ratio starts to decrease rapidly at \(\sim 1100\) K, where copper desorbs from the “\(\beta\)” state. For 1 ML < \(\theta_{\text{Cu}} \leq 2\) ML, this rapid decrease of Auger intensity ratio occurs at \(\sim 1000\) K, where copper desorbs from the “\(\alpha\)” state. For \(\theta_{\text{Cu}} > 2\) ML, the Auger intensity ratio starts to drop at an even lower temperature, consistent with nucleation of the copper overlayer to form three-dimensional islands. It can be seen...
from fig. 3 that the thicker films begin to nucleate at progressively lower temperatures.

LEED observations were also made during copper deposition and annealing. Before copper deposition, a sharp $(1 \times 1)$ LEED pattern with low background intensity was obtained from the clean Rh(100) crystal. No new LEED pattern was observed upon copper deposition at 115 K up to a copper coverage of $\sim 1$ ML, except that the diffraction spots were broader and the background more intense. Annealing the crystal resulted in a sharpening of the diffraction spots and a reduction in the background intensity. After an anneal to 500–700 K, the LEED pattern approached the quality of clean Rh(100), concomitant with the appearance of the maximum in the Auger intensity ratio versus anneal temperature plots shown in fig. 3. Further annealing to higher temperatures did not create any new features in the LEED pattern. These observations suggest that in the submonolayer coverage regime the copper overlayer forms two-dimensional islands pseudomorphic with respect to the Rh(100) substrate.

For $\theta_{\text{Cu}}$ above $\sim 1.2$ ML, after deposition of copper and an anneal to 300 K to reduce the background intensity, satellite spots appeared around the $(1 \times 1)$ diffraction spots. An anneal to 500–700 K resulted in further sharpening of the LEED pattern. This satellite structure has been reported in many metal overlayer studies and is taken as evidence of epitaxial film growth [34,35].

For $\theta_{\text{Cu}} > 2$ ML in this study the quality of the LEED pattern was poor even after an anneal to relatively high temperatures ($> 700$ K).

### 3.2. Thermal desorption of CO

Fig. 4 presents a plot of the total thermal desorption peak area versus exposure for CO adsorption on Rh(100) pre-deposited with 0.87 ML of copper. It is apparent that at the initial stage of CO adsorption, the coverage increases linearly with exposure, indicating that a mobile precursor state is involved in the adsorption. A similar behavior was observed for CO adsorption on clean Rh(100) [10].

After thermal desorption of CO from Rh(100) pre-deposited with various amounts of copper, the substrate is free from any carbon residue as determined by AES. A carbonaceous layer observed by Santoni and Urban [36], following exposure of either Cu(110) or Cu(100) surfaces to a CO atmosphere, was not detected here.
Fig. 4. A plot of total thermal desorption peak area versus exposure time for CO adsorption on Rh(100) pre-deposited with 0.87 ML of copper.

Fig. 5 displays the thermal desorption spectra of a saturation coverage of CO from clean Rh(100) and Rh(100) pre-deposited with various amounts of copper. On clean Rh(100), the desorption spectrum has a major peak ($\beta_1$) at 490 K with a small shoulder on the low temperature side. This spectrum is consistent with previous thermal desorption studies of CO on Rh(100) [9,10]. After depositing an increasing amount of copper, the $\beta_1$ peak maximum shifts to lower temperature and its intensity decreases. At the same time, more CO desorption peaks appear at lower temperatures as shown in fig. 5. Peak $\alpha\beta$ around 275 K begins to develop at a very low copper coverage ($\theta_{Cu}$) and is the only Cu-related CO desorption feature observed following copper deposition to 0.18 ML. This feature grows with increasing copper coverage, reaches its maximum intensity at a $\theta_{Cu}$ of ~0.4 ML, and disappears near the completion of the first copper monolayer. This suggests that the $\alpha\beta$ feature likely corresponds to the desorption of CO adsorbed at the periphery of two-dimensional copper islands. On the other hand, peak $\alpha_1$ at ~240 K begins to appear at a slightly higher $\theta_{Cu}$ than the $\alpha\beta$ peak. The intensity of the $\alpha_1$ feature increases with increasing $\theta_{Cu}$ and reaches its maximum at a $\theta_{Cu}$ of 1 ML. It then attenuates with increasing $\theta_{Cu}$ and disappears at the completion of the second monolayer of copper. This suggests

Fig. 5. Thermal desorption spectra of saturation coverage of CO from clean Rh(100) and Rh(100) pre-deposited with various amounts of copper and annealed to 750 K prior to CO adsorption at 115 K. (a) For $\theta_{Cu} < 1$ ML. (b) For $\theta_{Cu} > 1$ ML.
Fig. 6. CO desorption temperatures from various adsorption states as a function of copper coverage.

that peak $\alpha_1$ likely corresponds to CO adsorbed onto two-dimensional islands of the first copper monolayer. Another peak $\alpha_2$ centered at $\sim 195$ K occurs as early as $\theta_{\text{Cu}} \sim 0.5$ ML. Although the $\alpha_2$ peak intensity is small at $\theta_{\text{Cu}} < 1$ ML, this feature grows rapidly at the expense of the $\alpha_1$ peak intensity at $\theta_{\text{Cu}} > 1$ ML. The $\alpha_2$ peak becomes the only apparent CO desorption peak at the completion of the second copper monolayer. A further increase of the copper coverage does not substantially change this CO thermal desorption feature, except perhaps to downshift the peak temperature by a few degrees. Therefore, the $\alpha_2$ feature can be

Fig. 7. CO thermal desorption peak area as a function of copper coverage. (●) Total area. (○) $\beta_1$ peak area above 323 K.

Fig. 8. Thermal desorption spectra of saturation coverage of CO from Rh(100) freshly deposited with various amounts of copper at 115 K. (a) For $\theta_{\text{Cu}} < 1$ ML. (b) For $\theta_{\text{Cu}} > 1$ ML.
identified as corresponding to CO desorption from the second monolayer of copper and from three-dimensional copper clusters.

The CO desorption temperatures from different states as a function of copper coverage are summarized in fig. 6. It can be seen that there is a large CO desorption peak temperature shift in the $\beta_1$ state with copper coverage, from 490 K on the clean Rh(100) surface to $\sim 410$ K on Rh(100) covered with approximately one monolayer copper. In contrast, the CO desorption temperatures in the $\alpha\beta$, $\alpha_1$, and $\alpha_2$ states remain essentially the same.

The total CO thermal desorption peak area decreases monotonically with increasing copper coverage up to $\theta_{Cu}$ of 1 ML and stays essentially constant for $\theta_{Cu}$ above 1 ML, as shown in fig. 7. A plot of the integral area above 323 K (the peak area of the $\beta_1$ state) versus the copper coverage (also shown in fig. 7) fits very well a straight line, and reaches zero at the completion of the first monolayer.

CO thermal desorption spectra (shown in fig. 8) from freshly deposited, unannealed copper overlayers were quite different from those from copper overlayers annealed to 750 K. Compared with the annealed spectra of fig. 5, the $\beta_1$ peak of fig. 8, due to CO desorbing from exposed Rh (100), has approximately the same peak position and intensity. However, the low temperature peaks, due to CO desorbing from the Cu–Rh interface and copper overlayers, have quite different characteristics from the analogous annealed overlayers. The features of the unannealed spectra are considerably broader than their annealed counterparts, their peak maxima are generally at higher temperatures and their peak shapes are less well-defined.

4. Discussion

The results indicate that on the Rh(100) surface, the copper overlayer growth follows the Frank–van der Merwe, i.e., layer-by-layer, mechanism at least to the third layer. For copper coverages below one monolayer, the copper grows in a dispersed mode forming two-dimensional islands pseudomorphic to the Rh(100) substrate. In the second layer, the copper shows a similar two-dimensional island growth mode, but with an epitaxial Cu(100) structure. Upon annealing, the copper bilayer is stable up to the copper desorption temperature, while the copper deposits beyond the second layer nucleate to form three-dimensional clusters on top of the copper bilayer. A recent XPS study on the Cu/Rh(100) system [29] has shown that two monolayers of copper on Rh(100) are stable up to 900 K (the highest annealing temperature), with no changes in the Cu(2p)/Rh(3d) XPS intensity ratio upon annealing. Annealing films with copper coverages of 5 and 15 ML from 300 to 900 K produced an appreciable reduction in the Cu(2p)/Rh(3d) XPS intensity ratio, attributable to the formation of three-dimensional islands of copper. These XPS observations are consistent with the results presented here. Furthermore, similar metal overlayer growth mechanisms have been observed for Cu/Rh(0001) [19,35], Cu/Pt(111) [34], and Fe/W(110) [37] systems.

Although the overall growth of the copper overlayer on Rh(100) follows a layer-by-layer mechanism, the low-temperature (115 K) preparation leads to a considerably more roughened surface than that found following a 750 K anneal. This is due in part to the limited mobility of copper atoms at 115 K. Upon annealing a copper film with $\theta_{Cu} \leq 2$ ML, the overlayer undergoes rearrangement to form a well-ordered structure, as evidenced by the increase in the Cu(60 eV)/Rh(302 eV) Auger peak intensity ratio and a sharpening of the LEED diffraction spots. This rearrangement also explains why the CO thermal desorption features from unannealed copper overlayers are wider and less well-defined, as shown in fig. 8. These evidently are the convolution of CO desorption peaks corresponding to various stages of rearrangement of the copper overlayer during desorption. For a copper overlayer with a coverage 0.5 ML $\leq \theta_{Cu} \leq 1$ ML, even after an anneal to 750 K, there are still some copper atoms on top of two-dimensional islands. These are evidenced by the appearance of the small $\alpha_2$ peak in the CO thermal desorption spectra shown in fig. 5a. The roughness of the unannealed films is also apparent for Cu/Ru(0001) in that the work-function change
(\(\Delta \phi\)) decreases more rapidly for the unannealed films compared to the annealed films [19].

It can be seen from fig. 5 that the adsorption of CO on the surface of the first copper monolayer is obviously affected very strongly by the underlying rhodium. CO thermal desorption from monolayer copper (the \(a_1\) peak) is at a temperature (240 K) 50 K higher than that from bulk copper, suggesting a considerably higher binding energy or a stabilization of the CO on the monolayer film. The magnitude of the CO stabilization implies that the electronic modification of the copper by the rhodium is significant and possibly observable with a band structure probe. In fact, for the Cu/Ru(0001) system on which CO bonding exhibits a similar strengthening [19], Houston et al. [38], using angle-resolved ultraviolet photoemission spectroscopy (ARUPS), observed a state 1.5 eV below the Fermi level. This state saturated at a copper coverage of 1 ML and appeared localized in the copper and outermost ruthenium layers. Combined with surface electronic structure calculations, these authors concluded that this state is the anti-bonding combination of a pair of Cu(3d)–Ru(4d)-derived interface states.

Although the nature of CO chemisorption has been a subject of intense research, both theoretical and experimental, for many years, there is not as yet a unified picture regarding the metal–CO bonding. The conventional model for CO adsorption on metals was originally proposed by Blyholder [39]. According to this model, metal–CO bonding takes place via electron transfer from the 5\(a\) orbital of CO to the unoccupied metal orbitals. This “forward” donation of electrons is accompanied by “backdonation” of electrons from occupied metal d\(\pi\) orbitals to the unoccupied 2\(\pi\) orbitals of CO. The 2\(\pi\) orbital couples with metal orbitals of \(\pi\)-symmetry to form a bonding and an anti-bonding level. Recently Heskett et al. [40] have investigated the relationship between the electronic and vibrational properties of CO adsorbed on metal surfaces as measured by UPS and by EELS or IRAS. These authors have suggested that the metal–CO bond is formed in the conventional forward- and back-donation manner in a strong adsorption system such as CO adsorbed on transition metals. In this case the 2\(\pi\) level is partially occupied in the neutral ground state of the adsorbed system. On the other hand, for weak adsorption systems, such as CO adsorbed on noble metals, the bonding results from the transfer of charge from the CO 5\(a\) orbital to the metal d\(\sigma\) orbital such that the 2\(\pi\) level is essentially unoccupied. More recently, Messmer et al. [41,42] have proposed a modified picture of the bonding of CO to transition metals suggesting that donation from the CO 5\(a\) orbital must entail donation from a full to an empty state in order to form a strong bond. Since copper has a configuration of d\(^{10}\)s, no completely empty states are available either in the d- or the s-levels. Thus bonding of CO to copper is thought to involve primarily metal p-state charge transfer into the 2\(\pi\) orbital of CO with little direct overlap between the CO orbitals and the metal d-states.

Based on the picture suggested by Messmer et al., Houston and co-workers [43] proposed that for the CO/Cu/Ru(0001) system, the level of bonding of CO to copper must depend upon the degree of 4s occupancy and, hence, upon the ionic character of the copper sites. From the ARUPS results of CO adsorption on 1 ML Cu/Ru(0001) and the analysis of the symmetries of the interface states and of their positions relative to the bulk bands of ruthenium, they concluded that the Cu–CO interaction did not involve any appreciable hybridization with metal d-orbitals. Rather this interaction results from the formation of a CO(5\(a\))–Cu(4s) bond arising from the polarization of the Cu(4s) orbitals away from the CO. They attributed the fact that CO bonds more strongly to 1 ML Cu/Ru(0001) compared to pure copper to the decrease in 4s charge density local to the copper surface sites when copper is adsorbed on the ruthenium substrate. These authors suggested that the removal of 4s charge could be due to: (1) the fact that copper is less electronegative than ruthenium and, thus, donates charge to the substrate, (2) 4s-state polarization away from the copper layer into the substrate in the presence of adsorbed CO, and (3) backdonation from copper p-states to CO [43].

The similarities between rhodium and ruthenium are noteworthy. For example, rhodium has an electronic configuration of d\(^{10}\)s compared with d\(^{10}\)s
of ruthenium and is also more electronegative than copper. Thus a similar polarization and electronic charge transfer of the Cu(4s) orbitals in the CO/Cu/Rh(100) system is anticipated. This, in turn, should result in an enhanced Cu–CO bonding for CO adsorbed on 1 ML Cu/Rh(100). Indeed, in a recent XPS study of the system CO/Cu/Rh(100) [29], it was observed that adsorption of CO on copper films with submonolayer coverage produced a 0.7 eV shift toward a higher binding energy in the Cu(2p_{3/2}) peak position. This CO-induced Cu(2p_{3/2}) level shift is consistent with a reduction in the electron density of the copper adatoms upon CO adsorption. As the authors indicated, the decrease in copper electron density is probably a consequence of charge transfer from the copper adlayer to the substrate Rh(100) (induced by a repulsive interaction between the copper σ charge and the electrons in the 5σ orbital of CO [44]) and/or from the copper adatoms to the unoccupied 2π orbitals of the CO molecule (2π-backdonation). CO-induced Cu (2p_{3/2}) level shift toward a higher binding energy has also been observed for the CO/Cu/W(110) system [18].

Another plausible explanation for the enhanced Cu–CO bonding is based on the assumption that the chemisorption bond of CO on metals is dominated by the transfer of electron density from occupied metal orbitals into the unoccupied 2π orbital of the CO molecule (2π-backdonation) [45–47]. A recent XPS study [29] has shown a reduction of 0.43 eV in the surface Cu(2p_{3/2}) core level binding energy for 1 ML Cu/Rh(100) with respect to that of the surface layer in Cu(100). Previous experimental results for Cu(100) have shown that the core levels and the valence d-band centroid of the surface atoms shift in the same direction with respect to the corresponding values for the bulk atoms [48]. Therefore a shift toward lower binding energy for the copper valence levels of the 1 ML Cu/Rh(100) system is anticipated. This shift could reduce the separation between the occupied valence bands of copper and the unoccupied 2π orbitals of the CO molecule, leading to an increase in the 2π-backdonation and a subsequent enhancement of the strength of the Cu–CO bonding with respect to Cu(100) [29].

The geometric factor, i.e., the distortion arising from the pseudomorphic growth of the first copper monolayer, also contributes to the electronic modification of the first copper overlayer. A pseudomorphic monolayer of copper on Rh(100) has an atomic density mismatch of 10%, i.e., the atomic density of the copper is 10% less than that on Cu(100) [49]. The Cu–Cu nearest-neighbor distance of 2.69 Å is substantially larger than the value of 2.56 Å observed in bulk copper. Thus, the effective coordination number of copper atoms in a copper monolayer on Rh(100) is lower than the coordination number of the first copper layer in Cu(100). In general, for atoms with d-bands more than half full, smaller surface core level binding energies are observed as the coordination number of the surface atoms decreases [50–52]. Therefore the reduction in the effective coordination number of copper atoms in the 1 ML Cu/Rh(100) may lead to a decrease in the Cu(2p_{3/2}) core level binding energy with respect to that of the surface atoms of Cu(100). As discussed above, this may result in the reduction of the separation between the occupied valence bands of copper and the unoccupied 2π orbitals of the CO molecule, hence in a stronger Cu–CO bond with respect to Cu(100) due to an increase in 2π-backdonation. Clearly the geometric and electronic properties are closely coupled.

It is shown in fig. 5 that for copper coverages ≥ 2 ML, the Cu/Rh(100) exhibits copper-like properties with respect to the chemisorption of CO. The geometry of multilayer copper films is very nearly that of bulk copper, thus implying the short-range nature of the electronic interactions between copper and rhodium.

In the thermal desorption spectra of CO shown in fig. 5a, the β1 peak area decreases linearly with copper coverage and drops to zero at the completion of the first copper monolayer, as displayed in fig. 7. A similar behavior has been observed for CO adsorption on Ag/Rh(100) [16], Cu/Rh(111) [17], and Pd/W(110) [53].

Although CO (at finite pressure) is close-packed on both Rh(100) and copper, the saturation coverage of CO on Rh(100) is slightly higher than that on copper. This higher density on Rh(100) arises because the Cu–CO bond energy is smaller than
the Rh–CO bond energy, therefore there is less energy to compensate the repulsive interactions between the CO molecules. In fact, the saturation coverage of CO on Rh(100) has been reported to be between 0.60 [10] and 0.83 ML [9], while that on Cu(100) and Cu(111) has been estimated to be 0.58 [54] and 0.52 ML [12], respectively. Moreover, the saturation coverage on copper can only be achieved at sufficiently low adsorption temperatures. For temperatures above 110 K (115 K was used in the present study) Raval et al. showed that for Cu(111) a CO saturation coverage would not be achieved even with a background exposure of $1 \times 10^{-5}$ Torr of CO [55]. This explains why the total CO thermal desorption peak area decreases monotonically with increasing copper coverage up to $\theta_{\text{Cu}}$ of 1 ML and remains virtually constant for $\theta_{\text{Cu}}$ above 1 ML, as shown in fig. 7.

5. Conclusions

This study has shown that:

1. Copper deposited onto a Rh(100) surface at 115 K grows in the Frank-van der Merwe mechanism at least to the third layer. The first monolayer of copper is pseudomorphic with respect to the Rh(100) substrate, while the second monolayer grows epitaxially with a Cu(100) structure.

2. The first two copper layers are stable toward annealing up to the desorption temperature, while the copper deposits in excess of two layers nucleate to form three-dimensional copper islands on top of the copper bilayer.

3. The thermal desorption temperature of CO on Cu/Rh(100) with copper coverages up to 1 ML is ca. 50 to 85 K higher than that on bulk copper. Both electronic and geometric factors contribute to the enhancement of the CO–Cu/Rh(100) bonding strength.

4. For copper coverage $\geq 2$ ML, the substrate is very copper-like with respect to CO chemisorption, indicating the short-range nature of the electronic interactions between copper and rhodium.

5. Pre-deposited copper atoms on the Rh(100) surface induce a weakening of the Rh–CO bond and block CO adsorption on a one-to-one basis.

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