THE STRUCTURAL AND CHEMISORPTIVE PROPERTIES OF ULTRATHIN COBALT OVERLAYERS ON W(110) AND W(100)

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The structure, stability, surface electronic properties, and chemisorptive properties of vapor-deposited cobalt overlayers (0-4 ML) on W(110) and W(100) have been studied by Auger electron spectroscopy (AES), low energy electron diffraction (LEED), work function changes (Δφ), and temperature programmed desorption (TPD) of cobalt, hydrogen, and carbon monoxide. The first layer of cobalt grows pseudomorphically with respect to the tungsten substrate, and is thermally stable to 1300 K. Second and subsequent layers grow layer-by-layer at 100 K, but form three-dimensional clusters above 400-500 K. The relative work functions of these surfaces are strongly dependent on temperature, cobalt coverage, and substrate geometry. The annealed pseudomorphic monolayer of Co/W(100) has a positive Δφ value (+155 mV), indicating a net electronic charge transfer from the tungsten to the cobalt. The chemisorptive properties of the cobalt overlayers are quite different from those of bulk cobalt surfaces, the former having new TPD features for hydrogen chemisorption and TPD features consistent with carbon monoxide dissociation. CO apparently dissociates on cobalt-tungsten interfacial sites and on the pseudomorphic monolayer of Co/W(100).

1. Introduction

Bimetallic catalysts demonstrate enhanced selectivity, activity, and poison resistance relative to their single-metal counterparts for reactions such as reforming and methanation [1–3]. Surface scientists have attempted to identify the chemical and structural properties which give rise to these catalytic
enhancements by studying thin, vapor-deposited metal overlayers on metal single crystals. Bauer [4] has reviewed the structural and electronic properties of metal overlayers on metal surfaces. Of particular interest are the papers of Bauer et al., which describe the structure of transition metal overlayers (Cu [5], Au [6], Ag [6], Pd [7,8]) on W(110) and W(100). These studies demonstrate the applications of AES, I.FED, Aϕ, and TPD to the study of the structure of metal overlayers on tungsten single crystals.

Understanding the surface properties of mixed-metal systems may ultimately lead to the tailoring of bimetallic catalysts for specific uses. Among the most successful surface science work to date on bimetallic overlay systems as models of supported bimetallic catalysts are the studies of copper overlayers on ruthenium single crystals [9–15]. These metal overlay studies showed that copper atoms adsorbed on ruthenium crystallite surfaces block hydrogenolysis sites and enhance dehydrogenation rates, thus improving selectivity in catalytic reforming reactions.

Spurred by the success of the metal/W and Cu/Ru studies, this (Sandia) laboratory recently initiated a survey of transition metal (Cr [16], Ni [17], Pd [18], Fe [19], Co) overlayers on W(110) and W(100). The overlayer metals were chosen for their range of atomic sizes and their importance as catalysts. Tungsten was chosen as the substrate metal because its refractory nature allows the thermal desorption of these overlayer metals. This survey is an attempt to decouple the roles of geometry (ensemble effects) and electronic structure (ligand effects) in surface chemistry by systematically altering both the substrate and overlayer lattice constants. Of principle concern is how the altered geometry and electronic structure of the overlayers affect the chemisorption and reaction of catalytically important molecules such as hydrogen and carbon monoxide.

The prior studies [16–18] have concluded that the first monolayer of metal assumes the lattice dimensions of the tungsten substrate. This pseudomorphic monolayer is thermally stable up to the desorption temperature of the metal. Second and subsequent layers form layer-by-layer at 100 K, but are thermally unstable, forming three-dimensional clusters during high-temperature annealing. Due to the smaller atomic size and lattice constants of the overlayer metals, the pseudomorphic monolayers are geometrically strained with respect to bulk metal surfaces, and are known as strained-metal overlayers (SMOLS) [17].

The chemisorptive and catalytic properties of strained-metal overlayers on tungsten surfaces have been found to be different from those of their bulk metal counterparts. The binding energy of CO on Cu/W(110) increases relative to Cu(111) [20], whereas the binding energy decreases on Ni/W(110) relative to Ni(111) [17]. On Pd/W(110), CO adsorption at 300 K drops to zero at 1 ML coverage of Pd [21]. Ethane hydrogenolysis rates increase with the increasing geometric strain of nickel overlayers on W(110) and W(100) [22].
This paper reports the first study of cobalt overlayers on tungsten single crystals and the adsorptions of H₂ and CO on these overlayers. Supported cobalt has been extensively studied as a catalyst for Fischer-Tropsch synthesis [23,24]. The effect of cobalt surface geometry on the Fischer-Tropsch reaction (its structure sensitivity) is still a matter of controversy and is considered an unresolved question [25]. The objective of this study was to investigate the effects of altering the geometry and electronics of cobalt surfaces by forming strained-metal overlayers on tungsten single crystals; and then comparing the cobalt overlayers’ structural and chemisorptive properties with those of bulk cobalt single crystals, and with other metal overlayer systems.

Because of the difficulty involved in cleaning cobalt surfaces (while still retaining single crystallinity), there have been relatively few studies performed on cobalt single crystals. Lambert et al. [26-28] studied the chemisorption of H₂ and CO on planer and stepped cobalt single crystals. They found that CO adsorbs molecularly on the close-packed Co(0001) surface but dissociates on the stepped Co(1012) surface. Papp [29,30] found molecular CO adsorption on Co(O001) and dissociative adsorption on Co(1120).

This paper describes the structure, stability, and chemisorptive properties of vapor-deposited cobalt overlayers (0–4 monolayers) on W(110) and W(100). The overlayers were characterized by Auger electron spectroscopy (AES), low energy electron diffraction (LEED), work function changes (Δφ), and temperature programmed desorption (TPD) of cobalt, hydrogen, and carbon monoxide.

2. Experimental

2.1. Metal overlayer preparation

The experiments were carried out in a previously described [17,31] conventional UHV surface analysis chamber which had a base pressure of 1 × 10⁻¹⁰ Torr. The sample could be cooled to 100 K by a liquid nitrogen circulating system, or resistively heated up to 1800 K. Temperatures of 1800–2300 K were attained by heating with an electron beam filament which was mounted directly behind the sample.

The tungsten single crystals were cleaned by heating in 2 × 10⁻⁸ Torr oxygen at 1500 K for 10 min, followed by annealing in vacuum at 2300 K for 1 min. This procedure was repeated until a clean surface was obtained as determined by Auger electron spectroscopy (AES).

The cobalt source was a sliver of polycrystalline Co wrapped with a 0.25 mm tungsten filament, which was mounted in a rotatable evaporator arm and resistively heated. The cobalt source was extensively outgassed at 1100–1200 K in vacuum to deplete the bulk of impurities. Cobalt was vapor-deposited
onto the tungsten crystals by rotating the evaporator arm in front of the crystal face, with the tungsten crystal at 100–120 K. The cobalt flux at the crystal surface was maintained at about $10^{13}$ atoms/cm$^2$·s. After dosing a sample with cobalt and flashing to 800 K (to desorb any CO), no impurities were detectable with AES. Annealing of the cobalt overlayers was performed in vacuum at 1100 K for 30 s.

2.2. Characterization methods

2.2.1. Apparatus

Auger electron spectra were obtained with a double pass cylindrical mirror analyzer with a coaxial electron gun operating at 2 keV and 0.5 μA. Standard four-grid low energy electron diffraction (LEED) optics were used to monitor two-dimensional surface ordering. Temperature programmed desorption (TPD) measurements were carried out by resistively heating the sample in front of a UTI quadrupole mass spectrometer with a linear temperature ramp of 10 K/s.

2.2.2. Buildup curves

Overlayer buildup curves were determined by dosing cobalt onto a 100 K tungsten crystal, measuring the AES Co(775 eV)/W(169 eV) ratio immediately after deposition and following an 1100 K anneal, and then thermally desorbing the cobalt to obtain the Co TPD area. This procedure was performed at various levels of cobalt coverage. The buildup curves were used to determine the cobalt coverage of overlayer surfaces. Coverage assignments have ±10% error limits.

2.2.3. Thermal stabilities and surface structures

Thermal stabilities and surface structures of the cobalt overlayers were determined by measuring AES intensity ratios and LEED patterns of surfaces after vacuum annealing to successively higher temperatures of an originally unannealed surface. AES ratio versus temperature curves and LEED structures were determined for monolayer and for three- or four-layer coverages.

2.2.4. Relative work function curves

Relative work function measurements were made by following the energy position of the onset of secondary electron emission during irradiation by the Auger electron gun. The sample was biased at a negative 10 V to simplify electron energy determination.

2.2.5 $H_2$ and CO chemisorption

Hydrogen and carbon monoxide were dosed onto the sample at 100–120 K using a stainless steel needle, which gave a local pressure enhancement of 20:1 over a background dose. Exposures reported are the approximate exposures at
the front face of the crystal. Unless otherwise noted, corrected gas exposures were 1 L. Most chemisorption measurements were performed after the deposited cobalt layers had been annealed.

3. Results

3.1. Structure of the cobalt overlayers

3.1.1. AES spectrum

Fig. 1 is a typical AES spectrum obtained from the Co/W system. This spectrum was taken after dosing cobalt onto the W(110) surface and annealing to 1100 K. The tungsten features are the peaks between 100 and 220 eV and between 320 and 420 eV; while the cobalt peaks are those between 600 and 800 eV. The Co(775 eV)/W(169 eV) peak-to-peak intensity ratio for this spectrum is about 0.5, which corresponds to one monolayer coverage of cobalt (see fig. 2).

3.1.2. Buildup curves

The buildup curves for cobalt on W(110) and W(100) are shown in fig. 2. The linear regions of the unannealed curves correspond to the two-dimensional growth of the first, second, and third cobalt monolayers. There are clear breaks in the linear regions at the completion of each monolayer. Annealing of the Co/W(110) samples has no effect on the AES ratio of the first monolayer, but significantly lowers the ratio for second and subsequent layers. The AES ratio for the first monolayer and about half of the second monolayer of Co/W(100) are not affected by annealing. Annealing does decrease the ratio for coverages above 1.5 ML.

![AES Spectrum](image-url)
For Co/W(110), the TPD area ratio of the first to second monolayer is 0.70. For Co/W(100), the TPD area ratio of the first to second monolayer is 0.68.

3.1.3. Thermal stability curves

Fig. 3 shows thermal stability curves for cobalt overlayers on W(110) and W(100). LEED patterns obtained at various positions on the curves are indicated on the figure.

The AES ratio of the 1 ML Co/W(110) surface does not change significantly up to the desorption temperature of monolayer cobalt (1300 K). At higher coverage (3 ML) there is an initial increase in AES ratio with temperature, until the sample reaches 500 K, where the ratio decreases dramatically.
The ratio levels off between 600 and 1200 K, after which the cobalt begins to desorb and the ratio rapidly drops to zero.

The thermal stability curves for Co/W(100) are similar to the Co/W(110) curves. At a coverage of 1 ML the AES ratio does not change until the cobalt begins to desorb. At 4 ML a large decrease in the AES ratio is observed beginning at 400 K followed by a flat region between 600 and 1300 K.

3.1.4. LEED patterns

Fig. 4 shows the ordered LEED patterns obtained from the various cobalt overlayers. Fig. 4a is the LEED pattern for clean W(110), while figs. 4b, 4c,
Fig. 4. LEED patterns obtained for (a) clean W(110); (b) 1.25 ML Co/W(110) (satellite pattern); (c) 0.75 ML Co/W(100) ((1 x 1) pattern); and (d) 3 ML Co/W(100) (c(2 x 2) pattern). All surfaces were annealed at 1100 K.
Fig. 4. Continued.
and 4d are the patterns for 1.25 ML Co/W(110), 0.75 ML Co/W(100), and 3 ML Co/W(100), all four samples of which were annealed at 1100 K.

For annealed surfaces with cobalt coverages less than 1 ML, the LEED patterns (e.g. fig. 4c) are unchanged from the diffraction patterns of clean W(110) and W(100). A \((1 \times 1)\) LEED pattern is also observed for the unannealed 1 ML Co/W(100) surface, although an increase in background intensity is observed, which decreases with increasing temperature.

At coverages above 1 ML, the LEED pattern of the unannealed Co/W(110) surface (not shown) develops satellite spots with \(1/8\) of the tungsten spacing in the bcc \([1\bar{1}0]\) direction. The satellite spot pattern is also observed after the large drop in AES ratio from 500–1300 K, as shown in fig. 4b. The background intensity is observed to be high at low temperatures and high coverages but the diffraction spots are sharpened and the background is decreased with increasing temperature. The \((1 \times 1)\) pattern returns once the cobalt is desorbed to coverages less than 1 ML.

Between 1 and 2 ML, both the unannealed and annealed Co/W(100) surfaces develop a well-ordered \(c(2 \times 2)\) LEED pattern. At higher coverages and low temperatures complex LEED patterns with high background intensities are observed for the Co/W(100) surface. Following the drop in AES ratio, the \(c(2 \times 2)\) LEED pattern appears again, as shown in fig. 4d. Once more, the LEED pattern returns to the \((1 \times 1)\) pattern after desorption to coverages below 1 ML.

### 3.1.5. Cobalt TPD

The TPD spectra for cobalt desorption from W(110) and W(100) at various cobalt coverages are shown in fig. 5. For both surfaces, a high temperature desorption peak appears initially at low coverage, which saturates at 1 ML coverage. This peak is centered at 1450 K for Co/W(110) and 1525 K for Co/W(100). The high temperature peak is broader on the W(100) surface. After 1 ML coverage is reached, a low temperature peak appears at about 1350 K which continues to grow in intensity with higher coverage.

### 3.1.6. Relative work function curves

Fig. 6 shows the effects of cobalt coverage on the relative work functions of the Co/W(110) and Co/W(100) surfaces. Both the unannealed (100 K) and annealed (1100 K) curves are given.

On the annealed Co/W(110) surface, the relative work function decreases almost linearly with coverage up to 1 ML. The minimum in the annealed surface work function curve is about \(-700\) mV, and occurs close to 1 ML coverage. Above 1 ML coverage the relative work function rapidly increases and then reaches a constant value of about \(-200\) mV at 1.25 ML. The unannealed surface curve has a similar shape, but a consistently lower work function than the annealed surface.
The relative work function for the Co/W(100) surface is a strong function of annealing temperature and coverage and is very different from the work function of Co/W(110). The work function of the unannealed surface increases with coverage to a maximum of +340 mV near 0.5 ML; it then decreases back to zero near 1 ML and increases to positive values above 1.5 ML. The work function of the annealed surface has almost the opposite shape, initially decreasing to −160 mV at 0.4 ML, then rapidly increasing to a maximum of +155 mV at 1 ML; above 1 ML the relative work function decreases and levels off at about −150 mV.

Fig. 5. TPD spectra for cobalt desorption from annealed (A) Co/W(110); and (B) Co/W(100) at various cobalt coverages.
Fig. 6. Relative work function ($\Delta \phi$) of the unannealed (100 K) and annealed (1100 K) surfaces of 
(A) Co/W(110); and (B) Co/W(100) as a function of cobalt coverage.

3.2. $H_2$ and CO chemisorption

3.2.1. $H_2$ TPD

Fig. 7 shows the TPD spectra for hydrogen chemisorption on annealed 
Co/W(110) and Co/W(100) at various cobalt coverages, and compares them 
with the TPD spectra for $H_2$ on Co(0001), W(110), and W(100). On 
Co/W(110), $H_2$ has three desorption features: (1) a relatively sharp peak at 
300 K which is maximum near 0.6 ML and disappears above 1 ML of Co, (2)
Fig. 7. TPD spectra for hydrogen desorption from annealed (1100 K) (A) Co/W(110); and (B) Co/W(100) at various cobalt coverages. TPD spectra for hydrogen on Co(0001), W(110), and W(100) were taken from refs. [17,27] and are not drawn to scale.

a peak at 370 K for coverages near 1 ML and above, and (3) a broad high-temperature peak at 550 K at all coverages.

H₂ desorption from Co/W(100) results in a very broad desorption peak with a peak maximum at 380 K for all coverages. The area of this peak is twice
as large as the combined areas of the Co/W(110) H₂ TPD peaks. This peak has small shoulders near 300 and 500 K at low and high Co coverages respectively.

3.2.2. CO TPD

Fig. 8 shows the TPD spectra for carbon monoxide chemisorption on annealed Co/W(110) and Co/W(100) at various cobalt coverages, and com-

![Graph A](image)

![Graph B](image)

Fig. 8. TPD spectra for carbon monoxide desorption from annealed (1100 K) (A) Co/W(110); and (B) Co/W(100) at various cobalt coverages. TPD spectra for CO on Co(0001), W(110), and W(100) were taken from refs. [17,26] and are not drawn to scale.
pares them with the TPD spectra for CO on Co(0001), W(110), and W(100). CO has TPD features at 280, 380, 800, and 920 K on the Co/W(110) surface. The principal peak occurs at 380 K with a shoulder at 280 K. For submonolayer surfaces small, broad desorption peaks are observed at 800 and 920 K. Above 1 ML coverage these high temperature peaks are not observed.

During CO desorption from Co/W(100), peaks are observed at 280, 380, and near 900 K. The high temperature peak is much larger for Co/W(100) relative to Co/W(110) and its peak maximum gradually shifts from 920 K at 0.2 ML to 870 K at 1 ML. Moreover, this high temperature peak is observed on the Co/W(100) surface with the same peak area for all coverages of cobalt greater than 1 ML.

A few CO chemisorption experiments were performed on unannealed Co/W(100) at multilayer coverages. In these tests (results not shown) the high temperature peak gradually decreases in area as coverage increases from 1 to 4 ML. At 4 ML the high temperature peak is only 1/4 of the size of the 1 ML peak.

The TPD spectra obtained by varying the exposure of CO to the annealed 1 ML Co/W(100) surface are shown in fig. 9. An MKS Baratron pressure gauge was used to carefully control the amount of CO dosed onto the crystal. At 0.02 L the CO adsorbs only in the high energy binding state (at about 870 K). Between 0.04 and 0.18 L both 380 and 870 K peaks appear. Above 0.36 L the 870 K peak saturates and the 280 K shoulder appears.

![Fig. 9. TPD spectra for carbon monoxide desorption from annealed (1100 K) 1 ML Co/W(100) at various exposures.](image-url)
4. Discussion

4.1. Structural properties of the cobalt overlayers

Cobalt has two metallurgical phases, a hexagonal close-packed (hcp) phase at low temperatures, and a face-centered cubic (fcc) phase above 723 K [32]. Cobalt is also in the fcc phase at low temperatures when particle sizes are small [33]. Therefore, cobalt single crystals are in the hcp phase, whereas supported cobalt catalysts have crystallites in the fcc phase. Tungsten has the more open body-centered cubic (bcc) crystal lattice and a larger atomic diameter than cobalt. Thin overlayers of cobalt on tungsten single crystals are thus expected to have surface geometry which is altered or strained with respect to bulk cobalt surfaces. The degree of strain should be greater on the more open W(100) surface than on the close-packed W(110) surface. The cobalt overlayers are also expected to be altered electronically by the tungsten substrates, because the stabilizing force for the formation of strained overlayers is the strong interaction between overlayer and substrate atoms.

The structure of the cobalt overlayers is similar to that of copper and nickel overlayers on the same tungsten substrates [5,17]. The shapes of the unannealed buildup curves (fig. 2) show that cobalt overlayer growth on W(110) and W(100) is Frank–van der Merwe or layer-by-layer at 100 K. The (1×1) LEED patterns found for submonolayer and monolayer coverages (fig. 4) are consistent with the first layer of cobalt assuming the lattice dimensions of the tungsten substrate crystals. Fig. 10 shows the geometry of these pseudomorphic monolayers of cobalt on W(110) and W(100), and compares them with the geometry of the corresponding bulk cobalt surfaces. The pseudomorphic monolayer of cobalt on W(110) has geometric strain in the hcp [110] direction, and has an atomic density 21% less than Co(0001) (Co(111) is identical to Co(0001)). The pseudomorphic monolayer of cobalt on W(100) has geometric strain in two directions (fcc [011] and fcc [011]), and an atomic density 45% less than Co(100). The cobalt monolayers are thermally stable until the desorption temperature of cobalt is reached (1300 K). The degree of strain in the pseudomorphic monolayers is important for determining the effect of geometry on the surface chemistry of cobalt.

Nickel monolayers on W(110) and W(100) also grow pseudomorphically and are thermally stable [17]. Since the fcc lattice spacing of cobalt and nickel differ by only 1% (2.51 versus 2.49 Å [34]), the pseudomorphic monolayers of these metals on tungsten surfaces have essentially identical geometry and the same degree of strain. Therefore, the diagrams in fig. 10 can apply to nickel as well as to cobalt. Interestingly, cobalt has been found to grow pseudomorphically on Ni(100) [35].

Second and subsequent layers of cobalt on W(110) and W(100) grow layer-by-layer at 100 K, but are thermally unstable. The initial increase in AES
The satellite spot LEED pattern observed for second and subsequent layers of Co on W(110) (fig. 4) indicates that these layers are relaxed to or near the Co(0001) lattice structure [5,17]. This is the same LEED pattern observed for multilayer coverages of Ni/W(110) [17,36] and Cu/W(110) [5,37,38]. The TPD area ratio of the first to second monolayer of 0.7, is close to the ratio of surface atomic densities of Co(0001) and W(110) of 0.78. The occurrence of
the satellite spot LEED pattern after high temperature annealing (fig. 4) indicates that these surfaces have some remaining areas of two-dimensional multilayer cobalt, in addition to the areas of three-dimensional cobalt clusters and exposed pseudomorphic layer.

Multilayer coverages of Co/W(100) begin three-dimensional clustering at 400 K, which is 100 K lower than for Co/W(110) (fig. 3). The lower temperature is probably the result of the more open geometry of W(100). The appearance of the c(2 x 2) LEED pattern for Co coverages above 1 ML (fig. 4) is quite interesting. This pattern has been observed for annealed submonolayer coverages of Cu [5], Ag [6], Au [6], Pd [8], and Pb [39] on W(100); which appears to be accompanied by some rearrangement of the W(100) substrate [4]. We observed only the (1 x 1) LEED pattern for submonolayer coverages of Co/W(100). Multilayer coverages of Cu/W(100) also give the c(2 x 2) pattern, which is best developed at 1.5 ML [5].

The c(2 x 2) overlayer pattern is commonly encountered for gas adsorbates on (100) surfaces [40]. Two specific examples are CO adsorption on W(100) [41] and Ni(100) [42]. The pattern results as a consequence of lateral repulsion between the adsorbed gas molecules. It is surprising that metal overlayers give this type of arrangement because lateral metal overlayer interactions are generally attractive. However, Bauer et al. found strong mutual lateral repulsion between Cu atoms adsorbed on W(100) [5].

It should be emphasized that about half of the second monolayer of Co/W(100) was thermally stable (fig. 2), and that the c(2 x 2) LEED pattern was observed in this region. There are a number of arrangements which can lead to a c(2 x 2) pattern, and some correspond to one-half monolayer coverage of adsorbate [43]. It appears therefore likely, that a half-monolayer of cobalt forms a thermally stable, ordered layer on top of the pseudomorphic monolayer of Co/W(100). Occupation of the pseudomorphic monolayer's four-fold hollow sites is one likely arrangement for this ordered layer.

Cobalt has two desorption states on W(110) and W(100) (fig. 5). The high temperature peak corresponds to desorption of the pseudomorphic monolayer, while the low temperature peak is for multilayer desorption, showing that the binding energy of cobalt to tungsten is higher than the sublimation energy of bulk cobalt. Submonolayer cobalt is more strongly bound to the W(100) surface than the W(110) surface. On both surfaces, the AES ratio at the first appearance of the low temperature desorption peak corresponds exactly with the AES ratio at the first break in the unannealed buildup curve. This result is further evidence for layer-by-layer buildup and supports the coverage assignments made in this paper. Desorption of cobalt from the W(110) surface exhibits apparent zero-order kinetics, both in the first monolayer and for the multilayer coverages. However, desorption kinetics for Co/W(100) are non-zero-order for all coverages. This difference is difficult to explain, but closely matches the results for desorption of copper from these same surfaces [5].
The relative work function curves (fig. 6) are a measure of the electronic interaction between adsorbed cobalt layers and the tungsten substrates. Negative values of $\Delta \phi$ indicate net electronic charge transfer from the adsorbate to the substrate, while positive values indicate transfer from the substrate to the adsorbate [44].

The work function curves of Co/W(110) are similar to those found for Cu [5] and Ni [36] on W(110). The minimum in the annealed $\Delta \phi$ curve is $-700$ mV for Co, while those for Cu and Ni are $-800$ and $-750$ mV respectively. The initial linear decrease in the Co curve indicates that lateral electronic interaction between cobalt atoms in the first layer may be weak [45]. The constant $\Delta \phi$ value of about $-200$ mV for annealed multilayer cobalt is very close to the difference in the work functions of W(110), 4.6 eV, and polycrystalline cobalt, 4.4 eV [46]. The work function of the unannealed surface is consistently lower than that of the annealed surface because annealing smooths the overlayers. Surface roughness decreases the work function of surfaces [4].

The shapes of the unannealed and annealed work function curves for Co/W(100) are quite different from each other and from the curves for Co/W(110). The magnitude of this latter difference is unexpected considering the geometric similarity between the W(110) and W(100) surfaces. However, the $\Delta \phi$ behavior of Co/W(100) is consistent with the results found for other transition metal overlayers on W(100). Indeed, the shapes of the $\Delta \phi$ curves for these other metals are almost identical to those for cobalt. For example, low temperature $\Delta \phi$ curves for Cu [5], Au [6] and Pd [8] on W(100) have positive maxima (at or below 1 ML coverage) in the range of 150 to 400 mV as does Co/W(100). Annealed $\Delta \phi$ curves for Cu [5], Au [6], Pd [8], and Fe [39] on W(100)
W(100) all have a negative minimum at some coverage less than 0.5 ML and a maximum near 1 ML coverage. These curves are compared with the $\Delta \phi$ curve for annealed cobalt in fig. 11. The maximum values are $+20$ mV for Cu, $+475$ mV for Au, $+300$ mV for Pd, $-200$ mV for Fe, and $+155$ mV for Co.

The difference in the electronic environments of the pseudomorphic monolayers of cobalt on W(110) and W(100) is striking. At 1 ML coverage and after annealing, $\Delta \phi$ of Co/W(110) is $-700$ mV, while $\Delta \phi$ of Co/W(100) is $+155$ mV. The pseudomorphic monolayer of cobalt on W(110) is therefore donating electronic charge to the tungsten, while the layer on W(100) is accepting charge. This electronic effect has significant implications for CO chemisorption on these surfaces, as described in the next section.

4.2. Chemisorption on the cobalt overlayers

The surface chemistry of the cobalt overlayers is quite different from the chemistry of bulk cobalt. Changes in chemisorptive properties occur primarily in the first monolayer, where the structural and electronic modifications are greatest. Some of these changes are seen on annealed multilayer surfaces, because annealing exposes areas of the pseudomorphic monolayer.

4.2.1. Hydrogen chemisorption

Thermal desorption of hydrogen from Co(0001) and from polycrystalline cobalt gives a peak centered at 370 K [27,47], as shown in fig. 7. Hydrogen has two new TPD features on Co/W(110), one at 300 K and the other at 550 K. The 300 K peak occurs only for coverages below 1 ML, and may be the result of hydrogen chemisorption on a cobalt-tungsten interfacial site. Above 1 ML coverage, all of the tungsten atoms are covered with cobalt, eliminating the possibility for interfacial sites.

The 550 K peak occurs for all coverages of cobalt on Co/W(110). We assign this peak to hydrogen chemisorption on the pseudomorphic monolayer of cobalt. The increased distance between adjacent cobalt atoms in the pseudomorphic layer, as opposed to Co(0001) (3.16 versus 2.51 Å), should make recombination of the dissociated hydrogen atoms more difficult, leading to the higher desorption temperature. The 370 K peak corresponds to hydrogen desorption from bulk cobalt. This peak is largest for coverages above 1 ML, so we assign it to desorption of hydrogen from three-dimensional cobalt clusters.

Hydrogen chemisorption on clean W(110) gives peaks at 425 and 525 K [17]. Most of the adsorption on the 0.2 ML Co/W(110) sample is the result of hydrogen bonded exclusively to exposed tungsten sites. The contribution of adsorption on tungsten sites decreases in the TPD spectra as cobalt coverage increases. The 550 K desorption peak is almost certainly not the result of
chemisorption on tungsten sites because this peak is largest at multilayer coverages of cobalt.

The TPD spectra for hydrogen desorption from Co/W(100) are centered at 380 K, but the large peak area, the broadness of the peak, and the shoulder near 500 K all indicate that there are also high temperature binding states for hydrogen on this surface. These high temperature states are probably associated with adsorption to the pseudomorphic cobalt layer, while the state at 300 K is assigned to a cobalt–tungsten interfacial site as with the Co/W(110) surface. The hydrogenation activity of metal surfaces is strongly related to their binding energy for hydrogen [48,49]. The existence of new binding states for hydrogen implies that the catalytic activity of the cobalt overlayers could be different from that of bulk cobalt surfaces.

4.2.2. Carbon monoxide chemisorption

Carbon monoxide adsorbs molecularly on Co(0001), giving a TPD peak maximum at 430 K [26,29]. Polycrystalline cobalt [50] and the stepped Co(1012) [28] and Co(1120) [30] surfaces adsorb CO molecularly at low temperatures, but dissociate some of the adsorbed CO molecules during thermal desorption. Apparently, step sites are required for CO dissociation on bulk cobalt surfaces, just as they are for nickel surfaces [51,52]. CO dissociation is a critical step in the methanation and Fischer–Tropsch reactions [53]. On polycrystalline cobalt a CO recombination TPD peak was observed at 600 K [50]; however, recombination peaks were found to occur at higher temperatures on a stepped nickel surface (850 K) [51], and on Fe(100) (800 K) [54].

The desorption peak at 380 K for CO TPD from Co/W(110) is attributed to molecularly adsorbed CO (fig. 8). The 280 K shoulder may result because of lateral repulsive interactions between molecularly adsorbed CO molecules. These peaks (at 280 and 380 K) mask the smaller 300 K molecular adsorption peak of CO on tungsten, expected for surfaces with submonolayer coverages of cobalt.

Of greater importance are the high temperature (700–950 K) desorption peaks found for submonolayer Co/W(110). These are logically a consequence of recombination of dissociated CO, though isotopic experiments were not done to confirm this. The CO dissociation is not occurring on exposed tungsten sites in these samples, since the peak areas associated with recombination peaks increase with increasing cobalt coverage and because CO recombination peaks for tungsten surfaces occur at higher temperatures. The dissociation is also not taking place on the pseudomorphic cobalt monolayer on W(110), since annealed multilayer surfaces (which have exposed areas of the pseudomorphic monolayer) do not give the high-temperature peaks. We therefore believe that CO dissociation takes place on submonolayer Co/W(110) at cobalt–tungsten interfacial sites. At 0.9 ML coverage, 10% of the adsorbed CO molecules dissociate before the desorption temperature is reached. However,
on the 1.3 ML Co/W(110) surface, on which cobalt completely covers the tungsten surface, there is no evidence of CO dissociation.

Carbon monoxide adsorption is affected even more dramatically on the Co/W(100) surface, as 25% of the adsorbed CO molecules dissociate before desorption. At low CO exposures, the dissociation sites fill first (fig. 9), and so are more energetically favorable than the molecular adsorption sites. In contrast to adsorption on Co/W(110), CO dissociates at coverages above 1 ML on Co/W(100), indicating that the pseudomorphic monolayer of Co/W(100) is active for the dissociation of CO. On the unannealed Co/W(100) surfaces, cobalt multilayers cover the pseudomorphic layer, decreasing the area of the high temperature recombination peak. Above 2 ML coverage the peak area on unannealed surfaces might be expected to go to zero. Apparently it does not, because the thermal desorption process exposes portions of the active pseudomorphic layer; this occurs because the cobalt overlayers are thermally unstable at the higher desorption temperatures.

It is very informative to compare the CO chemisorption behavior of Co/W surfaces with those of cobalt single crystals, nickel single crystals, and nickel overlayers on tungsten single crystals. Ni(111) and Co(0001) have very similar geometries but these planer surfaces do not dissociate CO; however, stepped surfaces of cobalt and nickel do dissociate CO [28,51]. Nickel forms pseudomorphic monolayers on W(110) and W(100) which are geometrically identical to the cobalt pseudomorphic monolayers (fig. 10). Of the four pseudomorphic monolayers; Ni/W(110), Ni/W(100), Co/W(110), and Co/W(100), only the last (Co/W(100)) has the ability to dissociate CO. This implies that CO dissociation on Co/W(100) is likely not a consequence of geometric strain.

We conclude that CO dissociation on the pseudomorphic monolayer of Co/W(100) results largely from the electronic interaction between the cobalt and the tungsten. The relative work function of the pseudomorphic monolayer of Co/W(100) is positive (+155 mV, fig. 6b), indicating that there is net electronic charge transfer from the tungsten substrate to the cobalt overlayer. During CO chemisorption, the cobalt can thus donate extra electron density to the CO antibonding 2π* orbital through π-backbonding [55-57]. This strengthens the metal–carbon bond and weakens the carbon–oxygen bond [57], which lowers the activation energy for CO dissociation [51]. Work function measurements [58] have shown that as a general rule, step sites also carry a surplus of negative charge, accounting for CO dissociation on stepped surfaces of cobalt and nickel. EELS and Δφ measurements of CO adsorption on Co/W(100) might be used to confirm the electronic effect for CO dissociation that we propose.

It has generally been found that electronic effects are very important in the binding and dissociation of CO on metal surfaces. Broden et al. [57] conclude that electronics are the primary factor determining the occurrence of CO dissociation among transition metals, while surface geometry has only a
second-order effect. It is generally accepted that electropositive additives such as potassium donate electron density to transition metal surfaces, increasing the rate of CO dissociation [53]. Wesner et al. [59] found that potassium promotes CO dissociation on cobalt foils. Hamadeh and Gomer [20] conclude that the new desorption peaks for CO adsorption on Cu/W(110) result from the electronic interaction of tungsten with copper. It would be interesting to test CO chemisorption on Pd/W(100) or Au/W(100), since these surfaces have positive \( \Delta \phi \)'s at 1 ML coverage, similar to Co/W(100) (fig. 11) and since Pd and Au surfaces do not dissociate CO.

Annealed surfaces of Co/W(100) with coverages less than 0.8 ML have negative relative work function values, but will dissociate CO. Therefore, CO dissociation also occurs on cobalt–tungsten interfacial sites of submonolayer Co/W(100), similar to the sites on submonolayer Co/W(110). As the cobalt coverage approaches 1 ML, the relative work function becomes positive and the cobalt overlayer atoms dissociate CO. This change in dissociation site may be the cause of the gradual shift in the peak maximum from 920 to 870 K for submonolayer coverages of Co/W(100).

Thus, by comparing the geometric, electronic, and chemisorptive properties of cobalt and nickel overlayers on W(110) and W(100) it is possible to decouple the roles of geometry and electronic structure as they apply to CO dissociation on these surfaces. The lower activation energy for CO dissociation on Co/W(100) predicts that the Fischer–Tropsch activity of this surface may differ from that of bulk cobalt surfaces [53].

5. Summary

(1) Cobalt forms strained pseudomorphic monolayers on W(110) and W(100), the structural and chemisorptive properties of which are quite different from those of bulk cobalt surfaces.

(2) Second and subsequent layers of cobalt grow layer-by-layer at 100 K, but are thermally unstable, forming three-dimensional clusters above 400–500 K. A half-monolayer of cobalt forms a thermally stable, \( c(2 \times 2) \) ordered overlayer on top of the pseudomorphic monolayer on Co/W(100).

(3) The relative work function of the Co/W surfaces is strongly dependent on temperature, cobalt coverage, and substrate geometry. The electronic environments of the two pseudomorphic monolayers are strikingly different, with net electronic donation from cobalt to tungsten for Co/W(110) and from tungsten to cobalt for Co/W(100).

(4) Two new binding states are identified for hydrogen chemisorption on Co/W; a low temperature cobalt–tungsten interfacial site for submonolayer coverages, and high temperature binding states for adsorption on the pseudomorphic monolayers.
(5) Carbon monoxide adsorbs both molecularly and dissociatively on the cobalt overlayers. Dissociation takes place on two types of sites; a cobalt–tungsten interfacial site at submonolayer coverages of Co/W(110) and Co/W(100), and on the pseudomorphic monolayer of Co/W(100).

(6) Comparison of the CO chemisorption results with those for Ni/W(100) suggests that CO dissociation on the pseudomorphic monolayer of Co/W(100) is a consequence of electronic interaction between cobalt and tungsten, rather than geometric strain of cobalt. Thus, structural and chemisorptive studies of metal overlayers on W(110) and W(100) are useful in decoupling the roles of geometry and electronic structure as they apply to CO dissociation and reaction.

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References