An X-ray photoelectron spectroscopic study of the electronic properties of ultrathin Ni films on Ru(0001) and Mo(110)

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The electronic properties of ultrathin films of Ni on Ru(0001) and Mo(110) have been studied using X-ray photoelectron spectroscopy (XPS). The effects of Ni coverage (film thickness) are investigated for both substrates as is the effect of surface annealing temperature for the Ru(0001) substrate. In addition the effects of CO and H₂ chemisorption on Ni-covered Mo(110) and CO chemisorption on Ni-covered Ru(0001) are examined. The results indicate that the atoms in 1 ML of Ni on Mo(110) are electronically perturbed with respect to Ni(100) surface atoms, while the electronic perturbation for a monolayer of Ni on Ru(0001) is minimal. There is qualitative agreement between the shifts measured in the core-level binding energies and the corresponding CO desorption temperatures. The shifts can be explained by: (1) variations in the Ni–Ni interactions caused by a change in geometry of Ni surface atoms on Ru(0001) or Mo(110) as compared to Ni(100), and (2) the effects of Ni–Ru and Ni–Mo interactions. The adsorption of CO and H₂ induces a decrease in the electron density of the Ni adlayers.

1. Introduction

Bimetallic systems are found in many cases to be superior to monometallic systems with respect to catalytic stability, selectivity and/or activity [1]. In recent years considerable effort has been expended using a variety of surface science techniques to understand these catalytic differences by addressing the physical, electronic and chemical properties of well-defined bimetallic surfaces [2–19]. As part of a continuing effort to understand the electronic interactions in bimetallic systems we have examined the interaction of ultrathin Ni films with Mo(110) and Ru(0001) using X-ray photoelectron spectroscopy (XPS). The effects of adsorbate coverage (film thickness) are investigated for both substrates as is the effect of surface annealing temperature for the Ru(0001) substrate. In addition, the effects of CO and H₂ chemisorption on Ni-covered Mo(110) and CO chemisorption on Ni-covered Ru(0001) are examined.

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The properties of ultrathin films of Ni on Ru(0001) have been previously investigated using several surface-sensitive techniques. For coverages of less than 1 ML at 100 K, low-energy electron diffraction (LEED) studies [5] indicate that the overlayer is dispersed and disordered. Upon subsequent annealing to 700 K the Ni overlayer forms two-dimensional (2D) islands pseudomorphic with respect to the Ru(0001) substrate. Auger electron spectroscopy (AES) results [5] indicate a layer-by-layer growth mechanism at 100 K, whereas layers in excess of 1 ML form three-dimensional (3D) islands upon annealing to 1100 K. A single Ni desorption peak at 1350 K is observed in the temperature-programmed desorption (TPD) spectrum of the overlayer [5]. This is in contrast to Ni TPD studies from other substrates which clearly show separated monolayer and multilayer metal desorption features [6,7,12]. Results of angle-resolved photoemission (ARUPS) studies [20] indicate the presence of interface and surface states, with the principal interface feature, located at the Fermi level, ~ 60% occupied.
The interaction of ultrathin films of Ni on Mo(110) has also been studied using a variety of surface techniques [6,7]. Studies using LEED [6] have shown that at submonolayer Ni coverages a rectangular structure incommensurate with respect to the Mo(110) lattice is formed. At 115 K [6] and at room temperature [7] the Ni adlayers are found to grow in a layer-by-layer fashion using AES. These studies also indicate that layers in excess of 1 ML begin to form 3D islands when annealed to 800 K. TPD [6,7] shows two separate Ni desorption peaks, a monolayer feature between 1400 and 1500 K and a multilayer feature with an onset at \( \sim 1300 \) K.

2. Experimental section

The experiments were performed in an ultrahigh vacuum chamber (base pressure \( \leq 4 \times 10^{-10} \) Torr) equipped with AES, XPS, LEED and TPD capabilities.

The Mo(110) and Ru(0001) crystals were mounted by spotwelding to Ta support leads that allowed resistive heating to 1600 K. An electron beam assembly provided capabilities for heating to 2300 K. The manipulator allowed cooling of the sample to 115 K. The temperature was monitored by a W-5\(^{\circ}\)Re/W-26\(^{\circ}\)Re thermocouple spotwelded to the sample edge. The surfaces were cleaned following procedures reported in the literature [21] with the cleanliness and long-range order verified by AES, XPS and LEED.

The Ni was vapor deposited (sample temperature \( \sim 350 \) K) by resistively heating a W filament wrapped with high-purity Ni wire. The Ni doser was thoroughly outgassed before evaporation. The surfaces were annealed to 500 K after dosing to remove any contaminants with no impurities detectable by AES or XPS. The Ni coverages were determined by TPD area analysis [5,6]. All adsorbate coverages are reported with respect to the number of substrate surface atoms (Ru(0001) = \( 1.57 \times 10^{15} \) atoms/cm\(^2\) and Mo(110) = \( 1.43 \times 10^{15} \) atoms/cm\(^2\)). One Ni atom per substrate atom corresponds to \( \theta_{\text{Ni}} = 1.0 \).

An Al K\(\alpha\) X-ray source was used to record the Ni(2p), Mo(3d), Ru(3d) and O(1s) XPS spectra in section 3. The O(1s) and Ni(2p) binding energies were determined by referencing against the 3d\(_{5/2}\) peak of Ru(0001) or Mo(110) and have an experimental error of \( \pm 0.03 \) eV. Detection was normal to the surface in XPS and AES.

3. Results

3.1. Ni on Ru(0001)

In fig. 1 representative spectra of the Ni(2p\(_{3/2}\)) XPS region for various Ni coverages on Ru(0001) are shown. The spectra were acquired after Ni deposition at \( \sim 350 \) K and subsequent annealing to 500 K. The Ni(2p\(_{3/2}\)) peak position is observed to shift from 852.75 eV for the 0.35 and 0.80 ML coverages to the bulk binding energy value of 853.05 eV at 30 ML. There is no observable change with coverage in the full width at half maximum (FWHM).
The binding energy of the Ni(2p\textsubscript{3/2}) peak maximum is plotted as a function of Ni coverage in fig. 2. Submonolayer coverages show no shift in peak position from 852.75 eV. This can be explained in terms of the formation of 2D islands of Ni [5] and has been observed for several other bimetallic systems [15–18]. Increasing the coverage over 1 ML shows a monotonic increase in the Ni(2p\textsubscript{3/2}) peak position up to 853.05 eV at ~ 5 ML. Increasing the Ni coverage further shows no change in the peak position.

Fig. 3 plots the binding energy of the Ni(2p\textsubscript{3/2}) peak position and the Ni(2p)/Ru(3d) XPS peak intensity ratio versus the annealing temperature for Ni coverages of 0.8, 3.5 and 15 ML. The spectra were taken after preparing the Ni films by vapor depositing at ~ 350 K and annealing for 2 min at the specified temperature. Coverages of less than 2 ML showed no change in binding energy and only slight decreases in the Ni/Ru intensity upon annealing to 1000 K. There is an appreciable drop in the Ni/Ru XPS intensity for the 3.5 and 15 ML Ni coverages upon annealing to 1100 and 1200 K, respectively. The peak position for these coverages decreases slightly in binding energy during annealing. The peak position of 3.5 ML of Ni upon annealing to 800 K has a binding energy that corresponds very nearly to that for 2 ML of unannealed Ni. The decrease in Ni/Ru XPS intensity and the shift in the Ni(2p\textsubscript{3/2}) binding energy can be attributed to the formation of 3D islands of Ni, resulting in a significant portion of the second monolayer exposed.

The Ni(2p\textsubscript{3/2}) XPS spectra for clean and CO-saturated Ni films (θ\textsubscript{Ni} = 0.5 and 1.6 ML) on Ru(0001) are shown in fig. 4. The clean spectra were taken after evaporating the Ni at ~ 350 K and subsequently annealing to 500 K. The CO-saturated surfaces were prepared by cooling the clean surfaces to ~ 130 K and dosing with 30 L of CO. The adsorption of CO was found to induce a shift of +0.4 eV in the Ni(2p\textsubscript{3/2}) peak position for Ni coverages of less than 1 ML. Ni coverages greater than 1 ML showed a decrease in the magnitude of the core-level shift with increasing Ni coverage. This relates directly to the reduced fraction of the overall Ni bonded to CO. The effect of CO adsorption on the Ni(2p\textsubscript{3/2}) binding energy of the Ni films was reversible. Upon heating the CO/Ni/Ru(0001) system to 500 K the CO desorbed and the Ni(2p\textsubscript{3/2}) peak position returned to the clean Ni/Ru(0001) binding energy. For submonolayer Ni on Ru(0001) the O(1s) XPS spectra for adsorbed CO were very broad suggesting adsorption of CO on both Ni and Ru sites.

3.2. Ni on Mo(110)

The Ni(2p\textsubscript{3/2}) XPS region for several coverages of Ni on Mo(110) is presented in fig. 5. The surfaces were prepared by depositing the Ni (sample temperature ~ 350 K) and annealing to 500 K to remove any contaminant CO. The spectra indi-
Fig. 4. Ni(2p3/2) XPS spectra for clean and CO saturated Ni on Ru(0001). The Ni was deposited at ~350 K and annealed to 500 K before dosing 30 L of CO at ~130 K.

cate a shift in the peak position from 852.80 eV for the 0.38 ML coverage to 852.95 eV at 1 ML, to a bulk binding energy of 853.05 eV at 20 ML. There is no observable change with Ni coverage in the FWHM.

The plot in fig. 6 displays the shift in the Ni(2p3/2) peak position binding energy as a function of Ni coverage. In contrast to other systems recently studied [15–18], where the binding energy remains constant at submonolayer coverages (due to the presence of 2D islands), the Ni/Mo(110) system shows an increase in binding energy even at submonolayer coverages. Possible explanations of this are that the Ni overlayers are not forming 2D islands or more likely that the binding energy changes are related to phase transitions within the overlayers. For the Ni/Mo(110) system phase transitions have recently been observed with LEED [7]. In addition, infrared absorbance spectroscopy (IRAS) of CO chemisorption has given evidence to these same phase transitions by monitoring the shifts in frequency of the CO bond [22]. Above coverages of 1 ML there is an increase in
the binding energy up to ~4 ML where a bulk binding energy of 853.05 eV is observed.

The effect of CO adsorption upon the Ni(2p_{3/2}) XPS spectra is shown for several Ni coverages (θ_{Ni} = 0.20, 0.66, 1.0 and 1.5 ML) on Mo(110) in fig. 7. The Ni films were prepared by depositing Ni onto the Mo(110) surface at a sample temperature of ~350 K after which the sample was heated to 500 K. After taking the clean spectra the sample was cooled to ~130 K and dosed with a 30 L CO exposure and the spectra for the CO saturated surfaces were acquired. There is a shift in binding energy of +0.60 eV between the Ni(2p_{3/2}) peak position of clean and CO-covered Ni for coverages of less than 1 ML. As the Ni coverage increases above 1 ML the shift in binding energy decreases in magnitude due to the increased contribution of the subsurface Ni atoms to the overall binding energy. Heating the sample to 500 K to desorb the CO from the Ni films returned the Ni(2p_{3/2}) binding energy to the clean Ni/Mo(110) values. As with Ni/Ru(0001) (see above) the O(1s) XPS spectra (not shown) for CO/Ni/Mo(110) indicated adsorption of CO on both Ni and Mo atoms up to θ_{Ni} = 1 ML.

In fig. 8 the clean and hydrogen covered Ni(2p_{3/2}) spectra for 0.22 and 1.08 ML of Ni on Mo(110) are shown. The sample was prepared as for the CO/Ni/Mo(110) system with the substitution of H₂ for CO. For coverages of 1.08 ML of Ni or less the hydrogen saturation induces a shift in peak position of +0.25 eV from that of the clean Ni/Mo(110) system. This is similar to the shifts of +0.35 and +0.20 eV observed for hydrogen saturation on low Cu coverages (less than 0.2 ML) for the Cu/Re(0001) [18] and Cu/Ru(0001) [19] systems, respectively. Desorbing the hydrogen by heating to 500 K returned the Ni(2p_{3/2}) peak to the clean Ni/Mo(110) binding energy.

4. Discussion

For transition metals, the binding energy of surface atoms is distinct from that of bulk atoms due to a reduction in coordination number of the surface atoms [23,24]. For Ni(100) the binding
The energy of surface atoms has been found to be 0.45 eV below that of the bulk atoms [25]. In Figs. 2 and 6 the binding energy observed for bulk coverages (30 ML of Ni on Ru(0001) and 20 ML of Ni on Mo(110)) is due to the contribution of both subsurface and surface atom layers to the XPS signal. This binding energy can be assumed to approximate the combined value for the surface and bulk atoms of Ni(100) (see Fig. 9) [16]. Thus if the Ni atoms in 1 ML of Ni/Ru(0001) or Ni/Mo(110) were unperturbed with respect to the surface Ni atoms of Ni(100), the binding energy shift between 1 ML Ni/Ru(0001) or Ni/Mo(110) and the bulk coverage in Figs. 2 and 6 would be close to -0.35 eV [16,25]. The observed shifts are -0.3 eV (Ni/Ru(0001)) and -0.1 eV (Ni/Mo(110)), indicating that the atoms in 1 ML of Ni on Ru(0001) or Mo(110) are perturbed +0.05 and +0.25 eV, respectively, from the surface atoms in Ni(100). It is likely that the Ni atoms in the first layer of Ni/Ru(0001) or Ni/Mo(110) are stabilized to varying degrees via charge transfer from the overlayer to the substrate.

The results in Fig. 9 show that the atoms in the first monolayer of Ni on Ru(0001) are only slightly perturbed (+0.05 eV) with respect to the surface atoms of Ni(100). The atomic density of a pseudo-morphic layer of Ni on Ru(0001) (1.57 X 10^{15} atoms/cm^2) is virtually identical to the surface atomic density of Ni(100) (1.61 X 10^{15} atoms/cm^2). This similarity in Ni density and binding energy suggests that the contribution of the overlayer-substrate interaction to the core level shift is minimal.

In contrast, a +0.25 eV shift in binding energy is observed for the first monolayer Ni atoms on Mo(110) compared to the surface atoms of Ni(100). LEED studies indicate that the first Ni overlayer, rather than growing pseudomorphic with respect to the Mo(110) substrate, exhibits a (7 x 2) structure [22]. Therefore the Ni atomic density for the first monolayer of Ni on Mo(110) lies between that of Mo(110) (1.43 X 10^{15} atoms/cm^2) and Ni(100) (1.61 X 10^{15} atoms/cm^2). The Ni–Ni nearest-neighbor distance then for Ni on Mo(110) is greater than that for Ni(100) surface atoms. For late transition metals, theoretical studies have shown that the surface core-level shifts relative to the bulk value will increase as the nearest-neighbor distance increases [23]. Thus the increase in nearest-neighbor distance for Ni on Mo(110) should lead to a decrease in the binding energy with respect to Ni(100) surface atoms. The observed binding energy increase must arise from electronic interactions between the overlayer Ni atoms and the Mo(110) substrate. Experimental measurements [7] show a decrease in the work function of Mo(110) upon deposition of 1 ML of Ni atoms, consistent with electron transfer from the occupied orbitals of the adlayer into the empty electronic states of Mo.

The XPS data show that the atoms in 1 ML of Ni supported on Mo(110) are electronically perturbed with respect to the surface atoms of Ni(100). Similar results have been seen for the Ni/W(110) system [16]. These electronic perturbations have been explained using a combination of two phenomena: (1) variations in the Ni–Ni interactions caused by a change in geometry of Ni atoms on W(110) or Mo(110) compared to Ni(100), and (2) the effects of Ni–W and Ni–Mo interactions.

Thermal desorption of 1 ML of Ni from Ru(0001) [5], W(110) [12] and Mo(110) [6,7] indicates a higher desorption temperature for the
Ni/Mo(110) and Ni/W(110) systems. This suggests that the admetal–substrate interaction in Ni–Mo and Ni–W is greater than that for Ni–Ru. In agreement with this, the relative perturbations found in the Ni(2p\textsubscript{x}) XPS spectra (see fig. 9 and ref. [16]) follow the trend: Ni/W(110) (+0.35 eV) > Ni/Mo(110) (+0.25 eV) > Ni/Ru(0001) (+0.05 eV). A similar ordering has been found for the perturbations of supported Pd monolayers [46], with the XPS shifts in the Pd systems being always larger than in the Ni systems: Pd/Mo(110) (+0.90 eV [45]) > Pd/W(110) (+0.80 eV [16]) > Pd/Re(0001) (+0.65 eV [45]) > Pd/Ru(0001) (+0.30 eV [45]). It appears that for supported monolayers of Ni and Pd (Group 10 metals) the admetal–substrate interaction increases as the transition-metal substrate “moves” from right to left in the periodic table [46]. Electron-rich metals like Pd and Ni transfer more charge as the number of valence electrons in the metal substrate decreases. The strongest perturbations are observed for bimetallic systems that involve “electron-rich + electron-poor” metal combinations [46].

The XPS data indicate that the overlayer electronic modifications induced by adsorption of Ni or Pd on second- and third-row transition metals are more significant for palladium than for nickel. The metallic radius of Pd (1.38 Å) is closer to the radii of the substrates than that of Ni (1.25 Å). A similar metallic radius of Pd and the substrate enhances the overlap between the occupied electronic orbitals of the admetal and the empty electronic bands of the substrate. This overlap leads to a larger transfer of electron density from the Pd adsorbate to the substrate which, in turn, produces a larger shift in the Pd XPS binding energy.

The adsorption of CO on transition metals can be explained using the Blyholder bonding mechanism [26,27]. This mechanism assumes that bonding occurs via donation of electron density from the occupied metal electronic levels into the CO\textsubscript{2\pi} molecular orbitals, and from the CO\textsubscript{5\sigma} molecular orbital into the unoccupied metal electronic levels. Recent theoretical studies [28–30] have suggested that the \pi component is more important in determining overall bond strength than the \sigma component.

Thermal desorption studies of CO adsorbed on monolayers of Ni supported over Ru(0001) [5] and Mo(110) [6] indicate that the CO desorbs at 50 K higher and 30 K lower, respectively, compared with CO desorbing from Ni(100). This would indicate that the separation between the occupied valence levels of Ni (at \textit{E}_\text{vb}, below the vacuum level) and the empty \textit{2\pi}\textsuperscript{*} orbitals of CO (\textit{E}_\text{2\pi}\textsuperscript{*}, at \textsim 1.8 eV above the vacuum level [31–33]) has been increased for Ni/Mo(110). This conclusion is based upon the assumption [34,35] that an increase in the \textit{E}_\text{2\pi}\textsuperscript{*}–\textit{E}_\text{vb} separation will lead to a reduction in the heat of adsorption of CO and a corresponding decrease in the strength of the CO–Ni bond. The exact positions of the core and valence levels of Ni in Ni/Mo(110) are unknown relative to the vacuum level. Experimental results for the Au/Pt(100) [14] system have indicated that the core-level and the valence d-band centroid of the surface atoms shift in the same direction with respect to the bulk atom states. Similar results have been obtained for other mixed-metal systems [36–38]. Using this approximation the results of fig. 9 suggest a shift of the valence levels of the Ni monolayer supported on Mo(110) towards higher binding energy, an increase in the \textit{E}_\text{2\pi}\textsuperscript{*}–\textit{E}_\text{vb} separation, and a decrease in the strength of the Ni–CO bond. This agrees well with the TPD results. The XPS and work-function measurements are consistent with transfer of electrons from the Ni monolayer to the Mo(110) substrate (see above). A partial positive charge on the Ni adatoms is consistent with a reduction in the availability of electron density to coordinate to CO via backbonding, and thus an overall weaker Ni–CO bond on Ni/Mo(110) compared to Ni(100).

According to the results in fig. 9, for 1 ML of Ni on Ru(0001) the valence levels should be essentially energetically equivalent to the valence levels of the surface atoms of Ni(100), suggesting similar Ni–CO bond strengths in each case. However, the CO desorption temperatures indicate the CO–Ni bonding to be somewhat more stable for the Ni/Ru(0001) system [5,15]. Clearly other effects related to valence–valence interactions between admetal and substrate and to “final state” effects can be important for the Ni/Ru(0001) system and
are not explicitly accounted for in the above arguments. The correlation between shifts in core-level binding energies and changes in CO desorption temperatures observed for many bimetallic systems [15, 45] is not found for Ni/Ru(0001). In this system valence–valence interactions, which need not lead to variations of the core-levels [45], may dominate the perturbation of the Ni–CO bonding, rather than overlayer–substrate charge transfer.

The results of fig. 4 indicated an increase in the Ni(2p$_{3/2}$) binding energy (+0.4 eV for Ni/Ru(0001) and +0.6 eV for Ni/Mo(110) monolayers) upon the adsorption of CO on the Ni adlayers. The increase in binding energy suggests a reduction in electron density of the Ni surface atoms upon CO adsorption. The decrease in Ni electron density likely results primarily from the transfer of charge density from the Ni surface atoms into the 2π* orbitals of the CO molecule. Results for Ni(100) [25] have also shown a shift of approximately +0.5 eV in the Ni(2p$_{3/2}$) peak position upon CO adsorption.

The adsorption of hydrogen into Ni films of less than 1.08 ML on Mo(110) (see fig. 8) induces a shift in the Ni(2p$_{3/2}$) binding energy of +0.25 eV. This value is similar to the shift found in the Cu(2p$_{3/2}$) peak position for hydrogen adsorption on Cu/Re(0001) [18] and Cu/Ru(0001) [19]. These shifts suggest a net transfer of charge from the Ni or Cu adlayers upon hydrogen adsorption and are consistent with theoretical studies indicating that hydrogen adsorbed on Ni will be an electron acceptor [43, 44].

The data in figs. 2 and 6 indicate that Ni films over 5 ML in thickness show no further change in the Ni(2p$_{3/2}$) binding energy, and thus are representative of bulk Ni. Theoretical calculations that show convergence of thin films to the bulk electronic structure at 3 to 4 ML [39–42]. Our XPS results do not reach bulk Ni binding energy values until 5 ML either because of contributions from the perturbed surface Ni atoms to the overall binding energy and/or imperfect layer-by-layer growth. The results presented here also imply that the Ni–Ru and Ni–Mo interactions are of short range in nature.

5. Conclusions

(1) Our results indicate that the atoms in 1 ML of Ni on Mo(110) show a large electronic perturbation with respect to the surface atoms of Ni(100), whereas the electronic perturbation for Ni$_{1.0}$/Ru(0001) is relatively small.

(2) There is qualitative agreement for the Ni/Mo(110) system between the observed shifts in core-level binding energies and the corresponding CO desorption temperatures, as has been found for several other bimetallic systems [15, 16].

(3) The observed core-level shifts for Ni/Mo(110) can be explained by: (a) variations in the Ni–Ni interactions caused by a change in geometry of Ni surface atoms on Mo(110) as compared to Ni(100), and (b) effects of the Ni–Mo interaction.

(4) A transfer of charge from the Ni overlayers to the adsorbate is found following the adsorption of CO or hydrogen.

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References