PHYSICAL REVIEW B VOLUME 35, NUMBER 8 15 MARCH 1987-I

Electronic structure and chemical properties of Pt overlayers on Nb(110)

Xiao-he Pan,* M. W. Ruckman, and Myron Strongin
Physics Department, Brookhaven National Laboratory, Upton, New York 11973-5000
(Received 10 October 1986)

Photoemission, low-energy electron diffraction, and Auger-electron spectroscopy have been used to study the growth of Pt overlayers on Nb(110) and to determine the effect of electronic structure and overlayer morphology on surface chemical activity. It is found that Pt forms first a commensurate structure and then an incommensurate monolayer, both of which have a modified electronic structure. The Pt partial density of states is centered -2.7 eV below the Fermi level E_F and has a reduced density of states at E_F. At nominal monolayer coverage the intensity of the modified Pt electronic states reached a maximum and no CO chemisorption was observed. Further deposition of Pt, above a couple of monolayers, produced a surface whose electronic structure and surface structure resembles Pt(111) and molecular chemisorption of CO on Pt was observed. Comparison of our results with data reported for Pd on other refractory metals shows that the interaction between the Pt metal overlayer and the Nb substrate produces similar chemical effects.

I. INTRODUCTION

Studies of metal overlayers deposited on single-crystal surfaces of other metals have attracted attention recently because of their interesting chemical and physical properties. Previous investigators[1-4] have shown that the chemical activity of the metal overlayers can be varied by interaction with the substrate. For example, CO does not chemisorb at room temperature on Ta(110),[1] or Au(111) (Ref. 3) surfaces covered by a Pd monolayer. Large increases in the rate of cyclohexene dehydrogenation to form benzene are observed for Pt(100) covered by a Au monolayer.[4] In some cases, the authors attributed the origin of the modified reactivity of the metal overlayers to modification of surface atomic structure, such as the introduction of large hollows between the overlayer atoms, or steps with edge atoms that are more reactive than atoms in the smoother plane.[4] On the other hand, the novel chemical behavior of the Pd monolayer can be also traced to modification of the surface electronic structure.[1-3] We believe that both the electronic and geometric structure of the overlayer play a very important role in modified surface chemical activity, but as we will demonstrate, we attribute the novel chemical activity of Pt overlayers to substrate-induced modification of the surface layer's valence-band electronic structure which superficially resembles that of a noble metal with a fully occupied *d* band.

In a previous experiment on Pd/Ta(110),[1] we observed that a Pd monolayer with an atomic structure identical to the Pd(111) surface, had a drastically reduced CO sticking coefficient at room temperature. When the temperature was reduced to the liquid-nitrogen point to induce CO adsorption, modification of the CO molecular orbitals showed that the CO metal chemical bond was weaker as evidenced by the transposition of the 1π-5σ levels and the strengthening of the 4σ-2π shakeup peak. Since the Pd monolayer starts to undergo a commensurate-incommensurate structural phase transition below monolayer coverage and thermal treatments of thick Pd films on Ta to temperatures excess of 700 °C generated a commensurate Pd monolayer, it was possible to test the effect of varying the atomic structure of the overlayer on electronic structure and chemisorption. We found there was no significant variation in either the Pd overlayer photoemission spectrum or CO sticking coefficient between the two surfaces.

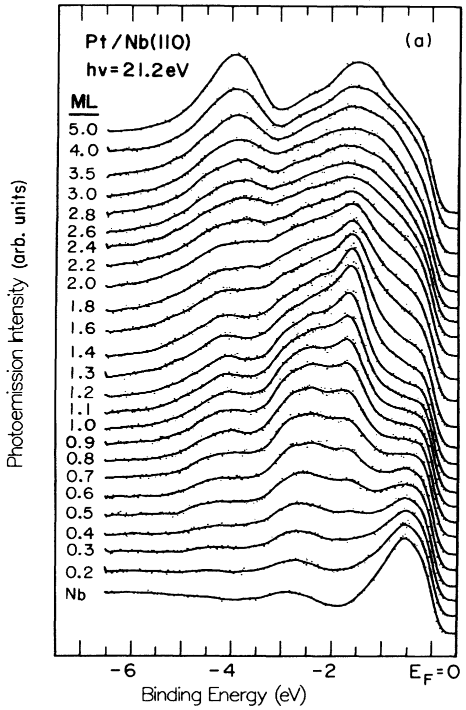
In this paper, we present results for Pt overlayers on Nb(110) and will demonstrate that Pt like Pd undergoes similar electronic changes when supported on a refractory metal and it will also be shown that Pt overlayers follow the same surface structural trends as Pd. The combined effect on the adsorption of CO is shown to be the same. Pt was chosen for this experiment because of its chemical and catalytic properties[5] and because the *d*-band structures and relative Pauling electronegativities of Pt and Nb suggest that strong interactions would occur between the Pt and Nb.

II. EXPERIMENTAL TECHNIQUES

The experiments were performed in a UHV system with a base pressure of about 7×10^{-11} Torr. A Nb(110) single-crystal substrate was prepared from 0.002-inch-thick polycrystalline niobium foil supplied by the Iowa State University Ames Laboratory. The foil strip was initially heated in vacuum and annealed at about 1000 °C in a low-pressure (10^{-6} Torr) oxygen atmosphere. Heating to temperatures of about 2200 °C, recrystallized the foil, removed bulk carbon as CO, and removed the surface oxide layer through evaporation. Temperature was measured with a optical pyrometer. The cleanliness of the sample was determined by Auger and photoemission spectroscopy (PES). Pt deposition was accomplished by evaporation from a resistively heated Pt filament which was initially degassed to ensure that the evaporation pressure would not exceed 3×10^{-10} Torr during evaporation. Pt coverages and evaporation rates were monitored using a thin film thickness monitor. The normal resolution of the thickness monitor was about 1.0 Å. Subangstrom coverages were produced by timed depositions after the evaporation rate was stabilized. Overlayer thicknesses were also checked by examining the relative intensities of the Nb 167 eV and Pt 64 eV Auger lines. Photoemission energy-distribution curves (EDC's) were measured using a double-pass cylindrical mirror analyzer. Photons at energies of 21.2 eV (He I) and 40.8 eV (He II) were supplied by a helium discharge lamp. During CO adsorption experiments, the carbon monoxide was admitted to the UHV system at a partial pressure at 2×10^{-8} Torr through a leak valve. At this partial pressure we found that an exposure of 20 langmuirs (L) CO gas was sufficient to saturate Nb and Pt metal surfaces. The purity of carbon monoxide was checked using a quadruple mass spectrometer.

III. RESULTS AND DISCUSSION

Monolayer and submonolayer coverages of Pt/Nb(110) ranging from 0.2 to 5 monolayers (ML) were characterized using Photoemission, Auger spectroscopy, and low-energy electron diffraction (LEED). Pt film coverages are expressed in "equivalent" Pt(111) monolayers which have a close-packed structure containing 1.5×10^{15} atoms/cm.[2] A factor of 0.44 ML per Å was used to convert from Angstroms to monolayers. Angle-integrated photoemission spectra for increasing coverages of Pt, obtained at photon energies of 21.2 and 40.8 eV at an angle of incidence of about 45° are shown in Fig. 1. Photoemission from clean Nb(110) is characterized by a by a large peak -0.4 eV below the Fermi level (E_F). This peak is due to a photoemission transition from a local minimum in the Σ_1 band where it crosses below E_F midway along the Σ direction.[6] A weaker peak at -3.1 eV can be attributed to transitions from the lowest Σ_1 band. The minimum at -1.8 eV results from a band gap between Σ_1 and Σ_2 bands. Additional photoemission states located between -0.4 and -1.8 eV are observed for polycrystalline or contaminated Nb surfaces.[7] Submonolayer Pt coverages generate new valence-band states located at -1.7, -2.3, -2.7, and -4.5 eV binding energy. The -2.3- and -2.7-eV peaks grow more rapidly with Pt coverage than the states at higher binding energy and reach a maximum value at a monolayer. The LEED patterns for small Pt coverages, Fig. 2(a), are identical to those of clean Nb(110) substrate but show increased background intensity. We believe the Pt atoms initially enter into random sites on the Nb(110) surface. Since the commensurate LEED pattern persists beyond 0.5-ML coverage it is likely that the Pt atoms agglomerate to form commensurate two-dimensional (2D) islands. Below monolayer Pt coverage, a set of ordered satellite spots appear in the LEED pattern [Fig. 2(b)] which are due to multiple scattering between an incommensurate Pt layer and the Nb(110) substrate. We believe this indicates that the Pt, like Pd/Nb(110),[8] has undergone a first-order structural phase transition from a commensurate to an incommensurate structure. At higher coverages, the Pt valence-band electronic structure undergoes further evolution. The 4.5-ev peak shifts about 0.7 eV to lower binding energy as Pt coverage approaches



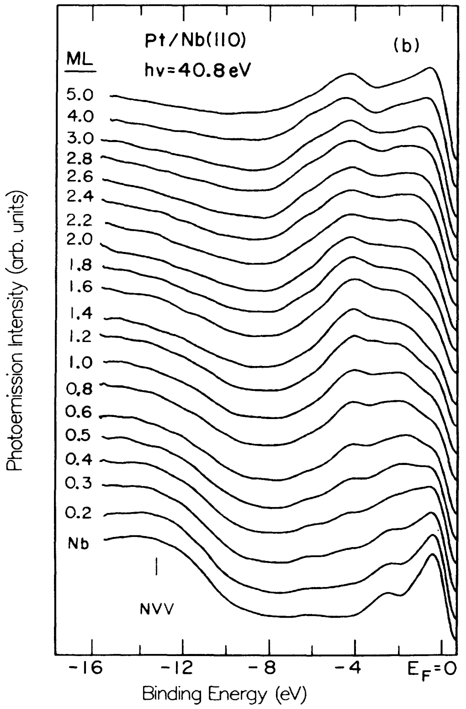


FIG. 1. Angle-integrated photoemission spectra obtained for various coverages of Pt on Nb(110) with photon energies of (a) 21.2 eV and (b) 40.8 eV.

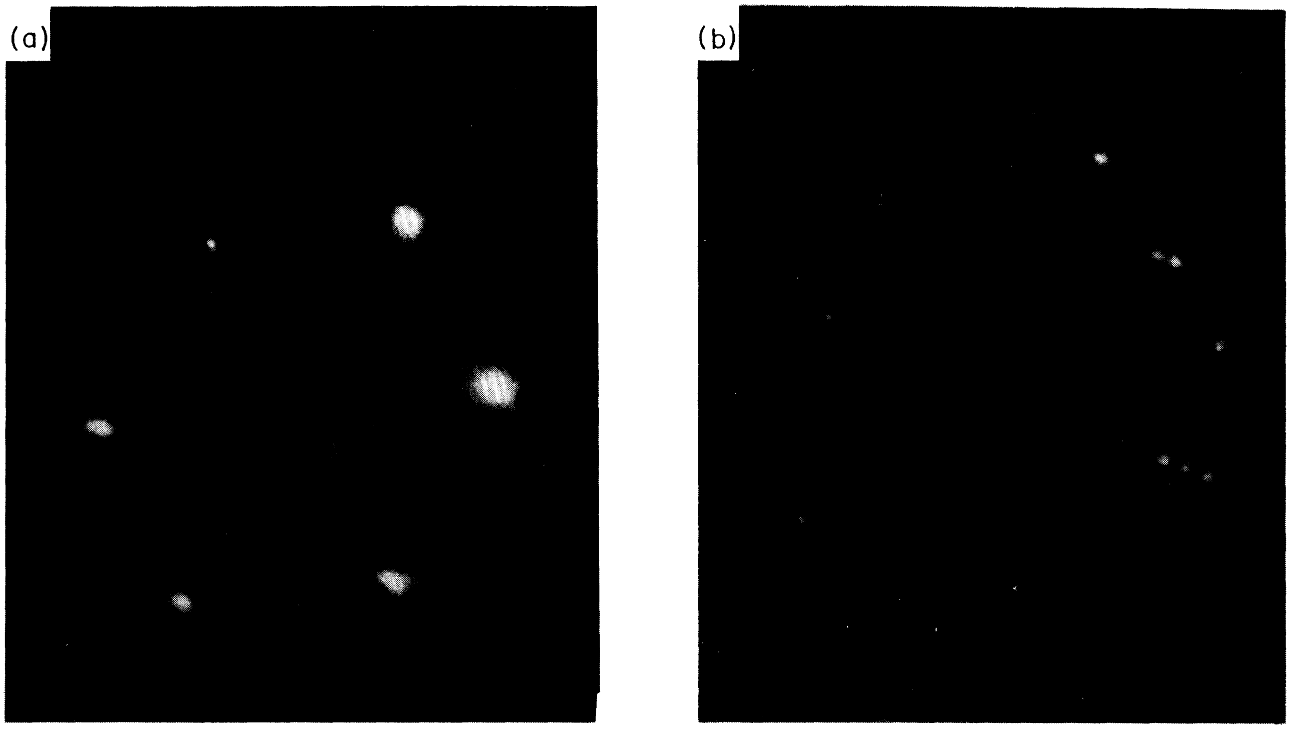


FIG. 2. LEED patterns seen for (a) Pt/Nb(110) for Pt coverages less than on 0.7 ML, and (b) for an incommensurate Pt/Nb(110) monolayer.

and exceeds a monolayer. The -1.7-eV peak grows faster and shifts ~ 0.2 eV to lower binding energy and the -2.3- and -2.7-eV peaks seen at low coverage disappear. The LEED patterns show that the ordered beat structure fades and the pattern characteristic of Pt(111) emerges. Beyond a few monolayers coverage, the -3.8-eV peak begins to grow more rapidly and finally reaches the same intensity as the -1.7-eV peak. The valence-band photoemission density of states is similar to that reported for single-crystal Pt(111).[9]

Correlation of the variation of valence-band electronic states with Pt coverage suggests that the -1.7- and -3.8-ev peaks, which only grow to significant intensities above two monolayers coverage, come from pure Pt metal. The peaks at energy -2.3 and -2.7 eV which appear at low Pt coverages are localized on the initial Pt monolayer. We suggest that these are Pt-Nb interfacial states formed by the hybridization of Pt d band with the s and d band of underlying Nb substrate. Further identification of these states with the underlying band structure can be drawn from analogy with theoretical calculations[10] and experimental results[10,11] for Pd/Nb(110). For Pd/Nb(110), the d_{xz-} and d_{yz-} derived states located near 3.0 eV were found to be split by 0.3 eV and similar results can be expected for Pt/Nb(110) which has the same C_2 point-group symmetry.[10] We tentatively identify the Pt states located at -2.3 and -2.7 eV as being derived from Pt and Nb d_{xz-} and d_{yz-} states.

Beyond 2.0-ML Pt coverage, a new state appears at -0.7-eV binding energy. This state grows continuously and saturates at about 5-ML Pt coverages.[12] The state at -0.7 is observed to be very sensitive to the presence of CO and H contamination. In photoemission spectra taken at 40.8 eV which are more surface sensitive, this state is larger and becomes the predominant d-band structure for clean Pt(111). We believe that this is a Pt surface resonance state and is analogous to a similar state observed for Pd.[12]

Our photoemission and LEED data suggest that Pt grows layer by layer. We examined the attenuation of the Nb MNN (167 eV) Auger line (Fig. 3) to test this hypothesis. If significant agglomeration of Pt occurs, the attenuation of the Nb line would be slower than expected for the accumulation of Pt in a uniform slab, which is an exponential of the form $\exp(-\theta/\lambda)$. In Fig. 3(a), we plot the attenuation of the Nb substrate component logarithmically and find that the Nb signal decreases exponentially with a $1/e$ escape depth of ~ 5.5 Å. The escape depth is consistent with the Seah and Dench[13] value expected for 167-eV Auger electrons.

During the photoemission experiments, we also applied a battery to measure the work function of Pt overlayers from the energy width from cutoff to the Fermi level in the photoemission spectrum. The dependence of the Pt overlayer work function as a function of Pt coverage is shown in Fig. 4. At very low Pt coverages (<0.1 ML), the work function decreases slightly. Previous workers[14] have pointed out that surface roughening, in part, due to

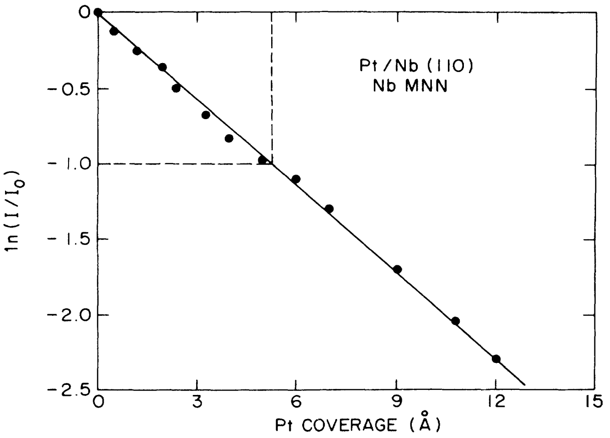


FIG. 3. Normalized attenuation curve for the Nb *MNN* (167 eV) Auger line plotted logarithmically as a function of Pt overlayer coverage. The $1/e$ attenuation is indicated by the dashed lines.

the random adsorption of adatoms can give rise to such a decrease. From ~0.1 to 0.75 ML the work function increases from 4.9 to 5.25 eV. At ~0.75 ML the work function begins to increase more rapidly and reaches a saturation value of 5.85 eV between 1.5 and 2 ML. The break in the work function trend line occurs near the coverage where the commensurate Pt layer becomes incommensurate. Distinct breaks in the work function trend upon changes in surface structure have been seen by Argile *et al.*[15] for Pb/Cu(111) and this was found to coincide with changes in the secondary election emission and Auger signal attenuation.

Thermal treatment of Pd on Nb(110) (Ref. 8) and Ta(110) (Ref. 16) showed that commensurate Pd monolayers could be formed by removing surface Pd from thicker layers. We also annealed selected Pt thin films at temperatures ranging from 600 °C to 1200 °C. Figure 5 shows the valence-band photoemission spectra at 21.2-eV photon energy for various annealing temperatures. The intensity of the Pt d states is reduced with increasing annealing temperature. The LEED patterns at these high temperatures showed first a diffuse Pt(111) pattern, and then no spots. No ordered Pt monolayer or surface compound was observed. By controlling the annealing time at temperatures ranging from 500 °C to 700 °C an "equivalent" monolayer composition as inferred from Auger line intensity ratios, could be achieved. We found a reduction of CO chemisorption on this annealed metal surface. This decreased chemical reactivity is due to alloy effects when the Pt overlayer is intermixed with the Nb(110) substrate after annealing.[17]

Figure 6 shows the effect of the exposure of 20-L CO on Nb(110) and selected Pt overlayers at 40.8-eV photon energy. We found that an exposure of 20-L CO saturates the surface. The spectrum of CO chemisorbed on Nb(110) surface shows that CO dissociates into individual C and O atoms producing carbon and oxygen bonding states at about -4.0- and -6.0-eV binding energy, respectively. According to previously published work,[18] CO dissociates on the Nb surface because the Nb valence d band contains partially filled d states to which electrons can be donated from CO 5σ orbitals and occupied d states

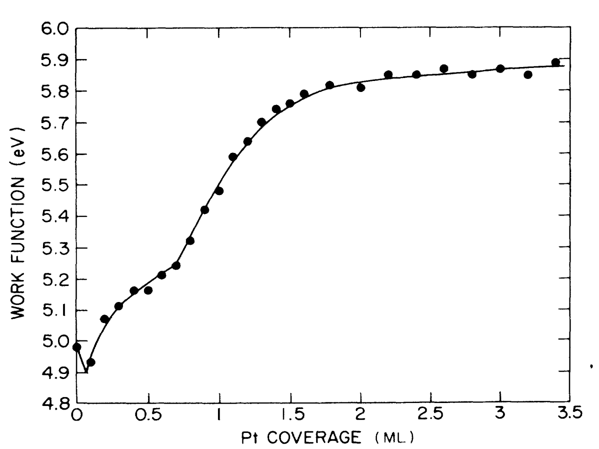


FIG. 4. Variation in the surface work function, as a function of Pt coverage for Pt/Nb(110).

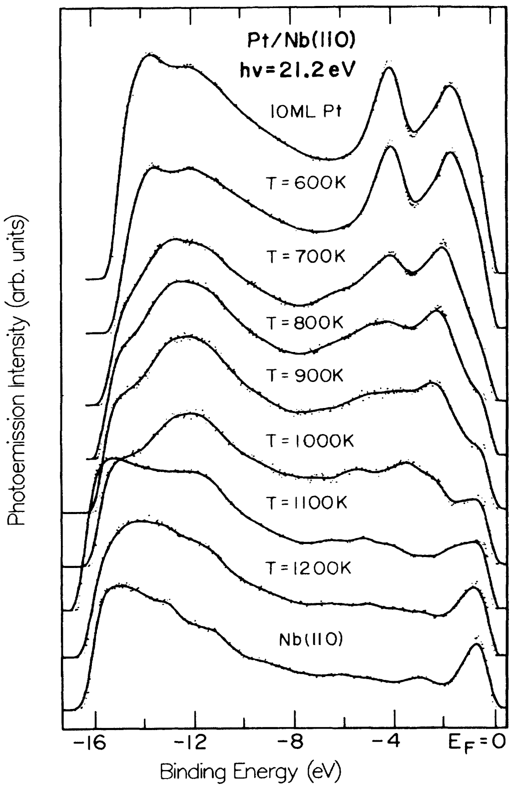


FIG. 5. Angle-integrated photoemission spectra taken at 21.2 eV for a Pt (10 ML) film annealed at temperatures from 600 to 1200 K.

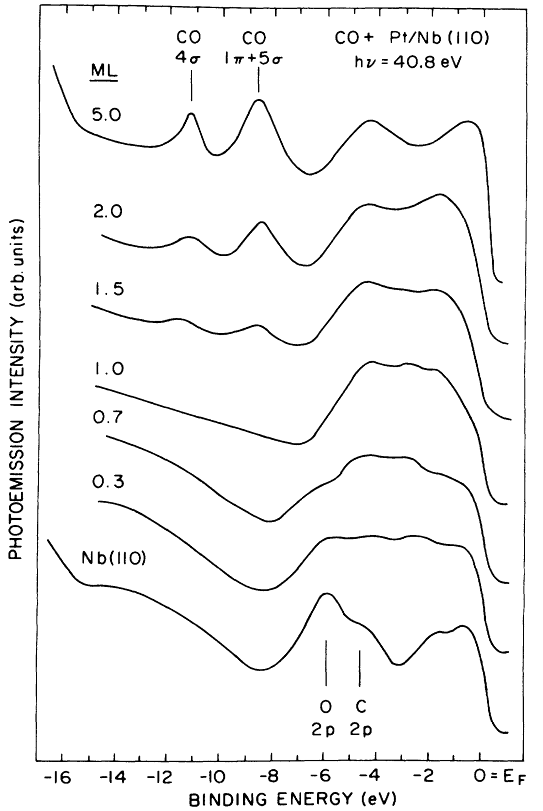


FIG. 6. Angle-integrated photoemission spectra taken for selected Pt coverages on Nb(110) after exposure to 20-L CO gas taken at 40.8-eV photon energy.

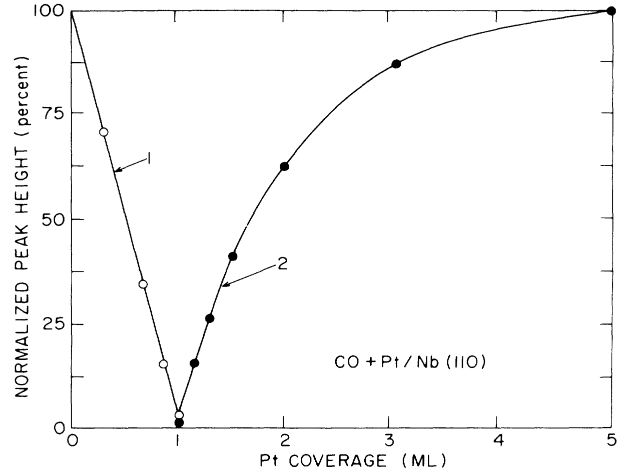


FIG. 7. Coverage of CO on selected Pt overlayers on Ta(110) after exposure to 20 L CO. [1 langmuir (L) $\equiv 10^{-6}$ Torr sec.] Approximate CO coverage is determined using the height of the CO derived photoemission features. Below monolayer coverage the combined C + O peaks (curve 1) are plotted. Above monolayer coverage the CO $1\pi+5\sigma$ peak (curve 2) is plotted.

from which electrons can be back-donated to the unoccupied molecular $2\pi^*$ level. The resulting partial occupancy of the antibonding level weakens the CO bonds leading to dissociation at room temperature. Photoemission for CO on Pt surfaces is completely different. Peaks attributable to molecular CO, namely the 4σ and 1π-5σ derived states are seen -11 and -8 eV below the Fermi level, respectively.[19,20] No CO derived photoemission features are seen for the EDC taken for a monolayer of Pt on Nb(110).

Figure 7 shows the saturation CO coverage relative to the coverage observed for Nb(110) below a monolayer and Pt(111) above a monolayer as a function of Pt coverage after an exposure to 20 L of CO. The CO coverage is inferred from the photoemission peak heights after background subtraction. At submonolayer coverages of Pt, a reduction in the amount of dissociative CO chemisorption was observed. The lack of molecular chemisorption by the Pt atoms indicates that the CO is unable to bond with Pt. We attribute the passive nature of the Pt to its electronic structure. The rehybridization of the Pd *d* band with the underlying Nb 4*d* and 5*s* derived band states reduces the width of the Pt *d* band and shifts its center of gravity to higher-binding energy which reduces the electronic density of states at the E_F. The reduction in the density of states near E_F means that fewer electrons reside in the highest-energy states that typically participate in forming chemical bonds with adsorbates. At monolayer coverage, when a Pt layer covers the surface, no CO chemisorption was observed. It is possible that some Pt atoms reside in the second layer as the Pt coverage approaches a monolayer. However, there are not enough Pt atoms in the second layer to show significant CO chemisorption which would be reflected in the photoemission spectra. Beyond a monolayer Pt coverage, pure Pt features start to appear and molecular CO adsorption begins. At 5-ML coverage, the overlayer shows only the Pt(111) character and molecular CO features. It should be mentioned here that the structure of the inert Pt monolayer is virtually identical to the five monolayer Pt film which readily chemisorbes CO molecules at room temperature. The key point is that the Pt monolayer undergoes changes in the electronic structure which reduces its ability to form bonds with the CO molecules which are strong enough to retain CO on the surface at room temperature.

IV. CONCLUSIONS

To summarize, we have studied the growth of thin Pt layers on Nb(110) at room temperature and find that the Pt atoms initially form commensurate two-dimensional islands which become incommensurate prior to monolayer coverage. The commensurate islands can be thought of as a highly strained fcc(111) layer. The Pt derived electronic structure for monolayer Pt/Nb(110) is highly modified from that of a close-packed Pt(111) surface, and is due to extensive Pt—Nb bonding across the Pt/Nb(110) interface. Modification of the Pt 5d states cannot be attributed to a change in Pt electronic configuration from metallic to atomic because Pt has a d^9s^1 atomic configuration which is similar to the metallic d and s-band occupations. The analogous modification of Pd 4d states for Pd/Nb(110) or Pd/Ta(110) could have been attributed to a change from the metallic d^9s^1 to the atomic d^{10} configuration. From the result for Pt, we conclude it is more likely that the change in shape of the Pd d-band results from rehybridization of Pd-Nb or Pd-Ta d and s states rather than configuration changes.

Further deposition creates a Pt(111) layer above the Nb(110) substrate. The electronic structure of the surface now converges to that observed for single-crystal Pt(111). The extensive rehybridization of the initial Pt monolayer has a great effect on the binding energy of CO on the Nb supported Pt monolayer surface. Reduction in the heat of adsorption of CO on Pt/Nb(110) is responsible for a near-zero sticking coefficient for CO at room temperature. The strong Pt-Nb interface interaction makes the Pt d band appear to be fully occupied and behave like a noble metal. The decreased chemical activity of Pt when the coverage approaches a monolayer can be accounted for by an inert Pt overlayer blocking the active Nb(110) substrate. No CO chemisorption was observed for monolayer coverages of Pt on Nb(110) confirming that the modified Pt-Nb(110) produces a chemically inert surface. When significant amounts of unmodified Pt appear at the surface, the chemical activity of the Pt overlayers resembles that of a Pt(111) surface.

ACKNOWLEDGMENTS

We are greatful to J. Davenport, P. D. Johnson, and Steve Hulbert for helpful discussions. We also thank F. Loeb and R. Raynis, who provided excellent technical support. This work was supported by the division of Materials Sciences, U. S. Department of Energy under Contract No. DE-AC02-76CH00016.

---

*Permanent address: Department of Physics, Queens College of the City University of New York, Flushing, NY 11367-0904.

[1] M. W. Ruckman, P. D. Johnson, and Myron Strongin, Phys. Rev. B **31**, 3405 (1985); M. Ruckman and M. Strongin, *ibid.* **29**, 7105 (1984).

[2] J. E. Houston, C. H. F. Peden, D. S. Blair, and D. W. Goodman, Surf. Sci. **167**, 427 (1986).

[3] Shen Xinyin, D. J. Frankel, J. C. Hermanson, G. J. Lapeyre, and R. J. Smith, Phys. Rev. B **32**, 2120 (1985).

[4] J. W. Sachlter, M. A. van Hove, J. P. Biberian, and G. A. Somorjai, Phys. Rev. Lett. **45**, 1601 (1980); M. Salmeron, S. Ferrer, M. Jazzar, and G. A. Somorjai, Phys. Rev. B **28**, (1983).

[5] S. I. Ginzburg, in *Analytical Chemistry of the Elements,* edited by A. P. Vinogradov (Wiley, New York, 1975).

[6] R. J. Smith, G. P. Williams, J. Colbert, M. Sagurton, and G. J. Lapeyre, Phys. Rev. B **22**, 1584 (1980).

[7] R. J. Smith, Phys. Rev. B **21**, 3131 (1980).

[8] M. Sagurton, M. Strongin, F. Jona, and J. Colbert, Phys. Rev. B **28**, 4075 (1983).

[9] N. Dahlback, P. O. Nilsson, and M. Pessa, Phys. Rev. B **19**, 5961 (1979); D. R. Lloyd, C. M. Quinn, and N. V. Richardson, Surf. Sci. **63**, 174 (1977).

[10] M. El-Batanouny, D. R. Hamann, S. R. Chubb, and J. W. Davenport, Phys. Rev. B **27**, 2575 (1983); V. Kumar and K. H. Bennemann, *ibid.* **28**, 3138 (1983).

[11] M. El-Batanouny, M. Strongin, and G. P. Williams, Phys. Rev. B **27**, 4580 (1983).

[12] S. -L. Weng and M. El-Batanouny, Phys. Rev. B **44**, 612 (1980).

[13] M. P. Seah and W. A. Dench, Surf. Interface Anal. **1**, 2 (1979).

[14] M. -G. Barthès-Labrousse and G. E. Rhead, Surf. Sci. **116**, 217 (1982).

[15] C. Argile, M. -G. Barthès-Labrousse, and G. E. Rhead, Surf. Sci. **138**, 181 (1984).

[16] M. W. Ruckman, V. Murgai, and Myron Strongin, Phys. Rev. B **34**, 6759 (1986).

[17] K. Besocke and H. Wagner, Phys. Rev. B **8**, 4597 (1973).

[18] G. Brodén, T. N. Rhodin, C. Brucker, R. Benbow, and Z. Hurych, Surf. Sci. **59**, 593 (1976); T. Engel and G. Ertl, Adv. Catal. **28**, 1 (1979).

[19] C. F. Brucker and T. N. Rhodin, Surf Sci **86**, 638 (1979).

[20] J. N. Miller, I. Lindau and W. E. Spicer, Surf. Sci. **111**, 595 (1981).

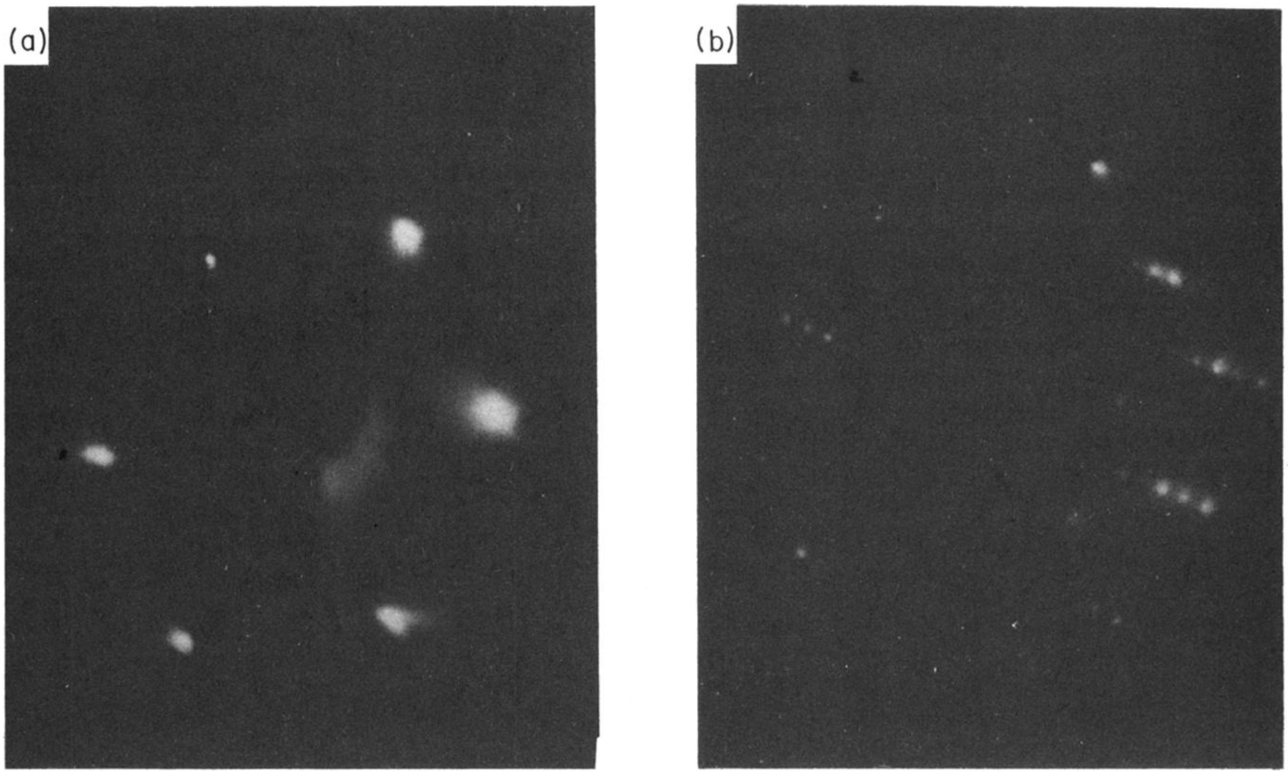


FIG. 2. LEED patterns seen for (a) Pt/Nb(110) for Pt coverages less than on 0.7 ML, and (b) for an incommensurate Pt/Nb(110) monolayer.