Structure-induced electronic states for Hg overlayers on Ag(100)

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Angle-resolved photoemission was used to observe the electronic band structure of one and two monolayers of Hg on Ag(100). Evidence for new Hg electronic states and band structure arising from the hybridization of the atomic $5d_{5/2}$ orbitals is presented. Low-energy electron diffraction results indicate that the Hg overlayers assume the face-centered-cubic (fcc) structure of the Ag(100) substrate, which is not the natural (rhombohedral) structure of bulk Hg. The new electronic states are induced as a result of the bonding of Hg atoms with adjacent metal atoms.

The study of thin (1–10 monolayers) metallic overlayers has become increasingly popular.[1] For most metallic adsorbates, there is a substantial (≥ 2 eV or 200 kJ/mol) heat of adsorption and a strong chemisorption bond between substrate and adlayer.[2] The study of weakly chemisorbed systems, although less widely investigated than strong chemisorption, has already revealed interesting phenomena including reversible melting and effects of reduced dimensionality.[3]

The investigation reported here was directed toward the study of the weakly chemisorbed metallic overlayer system of Hg on Ag(100), a metallic adsorption system unusual in several respects. The aim of this study was to investigate possible electronic states resulting from the hybridization of sharp (narrow full width at half maximum) Hg d orbitals by angle-resolved photoemission. The spin-orbit-split d-state mercury yields narrow peaks in the photoemission spectra at binding energies of about 8 and 10 eV below the Fermi level. These binding energies are sufficiently large for the Hg $5d_{3/2}$ and $5d_{5/2}$ orbitals to be regarded as shallow core levels. The Hg $5d$ orbitals do not overlap the broad Ag(100) d band,[4] but the Ag and Hg d bands are close enough in binding energy for possible hybridization. The potential for observing new electronic structure of mercury arises from inducing a face-centered-cubic (fcc) structure in the Hg overlayer which is different from the natural rhombohedral structure of solid mercury, and from the possibility of Hg and Ag d-band mixing.

Mercury adsorption on Ni(100) (Ref. 5), Fe(100) (Ref. 6), polycrystalline Au (Refs. 7–9), polycrystalline Ag (Ref. 7), polycrystalline Re (Ref. 7), polycrystalline Mo (Ref. 7), W and Mo field emitter tips (Ref. 10), W(100) (Refs. 11–13), and polycrystalline W (Ref. 14) have been reported. On both W(100) (Ref. 11) and Fe(100) (Ref 6), the Hg adlayer adopts the 1×1 crystal lattice of the substrate. The heat of adsorption of Hg on tungsten is about 208 kJ/mol (Refs. 11, 12, and 14) and about 106 kJ/mol on Fe(100).[6] Since Hg will adsorb on W and Fe at room temperature, but is not observed to adsorb on Ag(100) at room temperature for ambient pressures less than 10^{-8} Torr, it appears that the heat of adsorption for Hg on Ag(100) is comparable to or less than that observed for W and Fe. Certainly, since Hg is a monatomic vapor and does not cluser,[11] the heat of

adsorption of mercury on Ag(100) will be substantially less than for most metals.

The angle-resolved photoemission spectra were obtained using a photoelectron spectrometer system, described elsewhere,[15] also equipped with a retarding field analyzer for low-energy electron diffraction (LEED) and Auger electron spectroscopy. The light source was the Tantalus I synchrotron, operated by the University of Wisconsin, Madison, dispersed by a 3-m toroidal-grating monochromator. The energy resolution of the photoemission spectra, including the photon source, varied from 0.12 to 0.2 eV, full width at half maximum. The electric vector potential **A** of the incident light was parallel to the surface and along the Ag $\langle100\rangle$ direction throughout this work.

Following cleaning and annealing, the Ag(100) crystal was cooled to 89 K with the use of a liquid-nitrogen cold stage (as determined with a chromel-alumel thermocouple). Triply distilled Hg was admitted to the chamber via a standard variable-leak valve. The surface contamination was measured prior to and following each experiment with Auger electron and photoemission spectroscopy and found to be less than 1% overall.

The sticking coefficient for adsorption of Hg on Ag(100) at 89 K is constant as determined by the Hg $5d$-orbital photoemission intensities and Auger electron spectroscopy. Using the attenuation of the Ag d-band photoemission features with Hg exposure, and the electron mean free paths of Seah and Dench,[16] Penn,[17] and Powell,[18] we have determined that an Hg monolayer is present after 2.6 to 3.0 langmuirs (L, 1 L = 10^{-6} Torr sec) Hg exposure (uncorrected for ionization-gauge cross section and gauge position), at 89 K.

The development of the Hg-induced photoemission features and attenuation of the Ag photoemission features is shown for increasing Hg exposure in Fig. 1. For Hg coverages up to approximately half a monolayer, only the spin-orbit-split $5d_{5/2}$ and $5d_{3/2}$ doublet features are evident at $\bar{\Gamma}$ (normal emission). Similar features have been observed with Hg adsorption on gold foils[9] and Ni(100).[5] As the Hg coverage approaches one monolayer on Ag(100) (approximately 3 L Hg), a third feature appears with 7.2-eV binding energy at $\bar{\Gamma}$ (arrow, Fig. 1). This third Hg-induced feature continues to increase in intensity with increasing Hg adsorp-
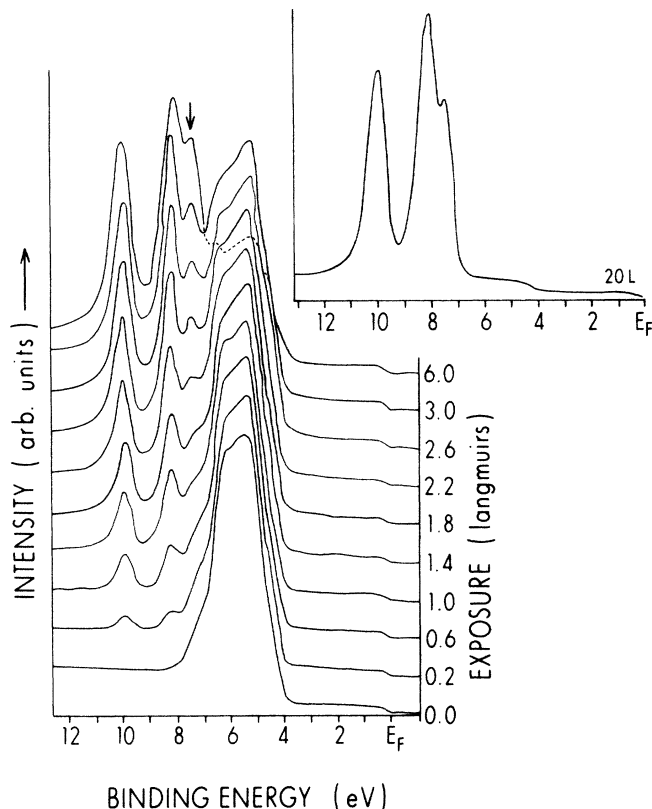
FIG. 1. Normal emission photoelectron energy distribution curves ($h\nu = 50$ eV) for various exposures of Hg (in langmuirs) on Ag(100). Arrow denotes new feature. Inset shows spectrum for 20 L exposure (~ 7 monolayer) of Hg.
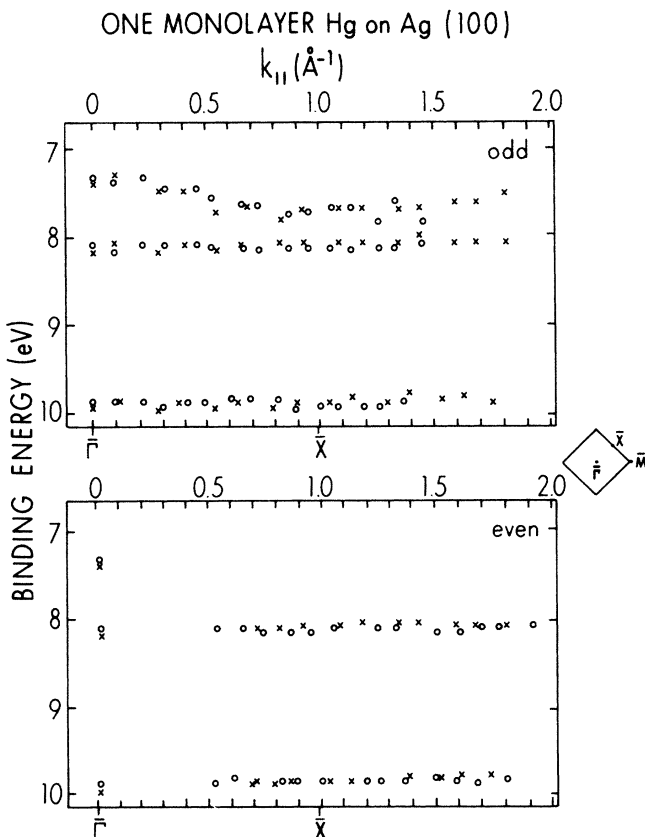

FIG. 2. Two-dimensional band structure of $p(1 \times 1)$ Hg on Ag(100). Photon energies corresponding to experimental results are denoted by O for $h\nu = 36$ eV and × for $h\nu = 50$ eV along the line $\bar{\Gamma}$-$\bar{X}$. Inset shows the surface Brillouin zone with the three high symmetry points ($\bar{\Gamma}, \bar{X}, \bar{M}$) of the SBZ.

tion and is observed with a thick adsorbed film of Hg on Ag(100) as shown in Fig. 1 (20 L, ~ 7 monolayers).

By collecting photoemission spectra at several photon energies over a range of emission angles, we have mapped out the binding energies of the three Hg-induced photoemission features as a function of $k_{\parallel}$ (electron momentum parallel to the surface) along the line of the surface Brillouin zone (SBZ) from $\bar{\Gamma}$ to $\bar{X}$ (see insert in Fig. 2). The results are presented in Figs. 2 and 3 for one and two monolayers of adsorbed Hg, respectively.

For one monolayer of Hg on Ag(100), the Hg-induced feature with a binding energy of 7.2 ± 0.1 eV at $\bar{\Gamma}$ disperses to a greater binding energy of 7.6 ± 0.1 eV at $\bar{X}$ in odd geometry. In even geometry, this feature cannot be observed away from $\bar{\Gamma}$.

For two monolayers of Hg on Ag(100), the Hg feature at 7.2 ± 0.1 eV at $\bar{\Gamma}$ is observed in both even and odd geometries. This feature disperses to greater binding energy in odd geometry (7.6 ± 0.1 eV at $\bar{X}$). In odd symmetry, the dispersion is symmetric about $\bar{X}$. Also, for odd symmetry, the dispersion and binding energies of the features resulting from the adsorption of Hg are independent of photon energy. By contrast, in even geometry the dispersion of the Hg-induced feature at ~ 7.2 eV is not symmetric about $\bar{X}$. Furthermore, dispersion for the ~ 7.2-eV band varies with photon energy. We conclude that for two monolayers, the third Hg feature exhibits "bulklike" behavior in even sym-

metry because the dispersion is not consistent with the surface Brillioun zone.

The desorption of Hg from Ag(100) at or below room temperature, and the absence of any adsorption with exposure to 10^{-8} Torr of Hg onto Ag(100) at room temperature, indicate that Hg is weakly bound to Ag(100). The Ag(100) photoemission features are surprisingly unaffected by Hg adsorption, apart from the attenuation of the Ag feature. The relative Ag(100) binding energies and intensities are retained at the high-symmetry points following Hg adsorption. This suggests that there is no strong hybridization of Hg and Ag orbitals and strong chemisorption bonds are not formed.

The two Hg-induced features at 8.0 ± 0.1 and 9.8 ± 0.1 eV binding energies do not disperse with changes in $k_{\parallel}$ or photon energy. Furthermore, these Hg-induced features have binding energies that remain unchanged with increasing Hg overlayer thickness (Fig. 1). This is the expected behavior for core levels of weakly bound adsorbates. We therefore assign the 8.0- and 9.8-eV-binding-energy features to the spin-orbit-split $5d_{5/2}$ and $5d_{3/2}$ orbitals. The spin-orbit splitting of these orbits is consistent with other measurements.[19-22]

The third Hg-induced feature with a 7.2-eV binding energy at $\bar{\Gamma}$ must now be explained. Various authors[22,23] have
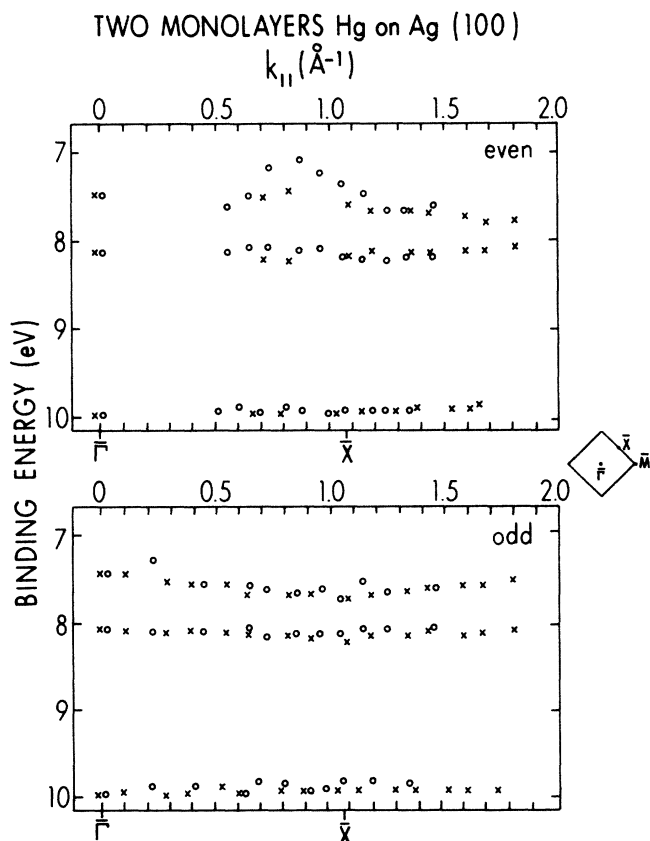
FIG. 3. Two-dimensional band structure of epitaxial Hg on Ag(100) along the line $\bar{\Gamma}$-$\bar{X}$. Experimental results are denoted for $h\nu = 36$ eV (o) and $h\nu = 50$ eV (×).

quench, the Ag(100) surface states. In fact, Hg overlayers affect the Ag(100) surface states surprisingly little. Thus while interfacial hybridization between Hg and Ag cannot be eliminated, the 7.2-eV binding energy feature is unlikely to be a result of an interface state, given that increasing Hg coverage does not diminish this feature.

The third low-binding-energy feature at $\bar{\Gamma}$ in odd geometry with one monolayer and the evolution of this feature in even and odd geometries is consistent with the development of an Hg band structure due to the epitaxial fcc structure the Hg is forced to assume.

As indicated by LEED, Hg adsorption results in a 1×1 overlayer for one and two monolayers of Hg on Ag(100). The Hg feature disperses symmetrically about $\bar{\Gamma}$ and $\bar{X}$ further supporting this observation (apart from the even 7.2-eV band for two monolayers). Symmetry thus restricts the Hg-induced features for one and two monolayers to be of Δ_1 or Δ_5 symmetry at $\bar{\Gamma}$. Dipole selection rules dictate that the observed Hg bonds be of Δ_5 symmetry at $\bar{\Gamma}$. Appearance of an even band away from $\bar{\Gamma}$ for two monolayers that is not symmetric about $\bar{X}$ is consistent with development of bulk band structure.

For Hg adsorption of more than two monolayers, LEED indicates that the 1×1 fcc overlayer structure is imperfectly preserved, and disorder increases with increasing exposure until by four monolayers long-range order does not exist. With an Hg overlayer of 6.5 to 8 monolayers [20 L Hg exposure on Ag(100) at 89 K] and adlayer structure is quite different from the fcc 1×1 structure.[20] Because of the changes in the Hg overlayer structure above two monolayers, the dispersion of the 7.2-eV binding energy Hg photoemission feature cannot be determined. Despite the change in structure and the expected changes in electronic structure, the 7.2-eV feature does appear to be a result of Hg hybridization with adjacent Hg atoms to form a band. The formation of the hybrid Hg orbitals into intinerant states is also supported by recently observed interband transitions for thin films of Hg, forbidden for isolated Hg atoms.[26]

The Hg on Ag(100) system, then, is a weakly chemisorbed system in which the new (fcc) crystallographic structure the overlayer assumes is accompanied by new Hg-band-structure features arising out of Hg electronic states commonly regarded as core levels. This is a surprising and interesting result. Core levels, even shallow ones such as Hg possesses, are commonly viewed as virtually atomic. The evidence suggests that the combination of weak chemisorption and the induced fcc structure leads to this new band structure. We intend to investigate the behavior of this new Hg band under a variety of conditions, e.g., at various temperatures, e.g., melting temperature, on a variety of surfaces and substrate (Cu,Ag), and to determine the thermodynamic details of the chemisorption process.

observed further splittings of d-orbital energy levels in different systems beyond the spin-orbit splitting, apart from Ref. 13 no such further splitting has been observed for adsorbed or solid Hg. These additional d-orbital features have been explained by "crystal-field"[24] effects[22] or by the symmetry of the adsorbate site.[25] Neither of these possibilities is consistent with our observations. The 7.2-eV feature does not exist for very low coverages. Either a "crystal-field"-effect- or a symmetry-site-induced feature would, however, be expected at low coverages. The observed variations in relative intensity and binding energy for the low-binding-energy Hg-induced feature is also not consistent with crystal-field effects. A crystal-field effect might change in magnitude with exposure, but not symmetry; thus, since the 7.2-eV binding energy feature at $\bar{\Gamma}$ is observed in even and odd geometries away from $\bar{\Gamma}$ for two monolayers of Hg but is only observed in odd geometry (away from $\bar{\Gamma}$) for one monolayer of Hg, the crystal-field effect is not inducing this feature.

We also conclude that the Hg feature with a 7.2-eV binding energy at $\bar{\Gamma}$ is not an interface state. An interface state should be attentuated as the Hg coverage is doubled, while the reverse of this is observed to occur. The presence of an interface state should dramatically affect, and possibly

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