The influence of crystallographic order upon the electronic structure of thin mercury overlayers

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Thin (1–7 monolayer) well-ordered, disordered, and liquid Hg overlayers on Ag(100) have been investigated with angle resolved photoemission and low-energy electron diffraction. The well-ordered overlayers exhibit new electronic states as a result of the strained, cubic, overlayer crystallographic structure. The new electronic states depend upon the long-range crystallographic order of the overlayer, not simply the local crystallographic symmetry. The photoemission cross section and branching ratio of the 5d mercury states depends on the overlayer long-range crystallographic order and cannot be explained by photoelectron diffraction.

I. INTRODUCTION

Hg overlayers possess three salient advantages for studying the relationship between electronic and crystallographic structure. Hg is easily adsorbed on Ag(100) and under certain conditions forms ordered overlayers. The ordered Hg overlayers, which possess low melting temperatures, permit direct observation of the relationship between the degree of crystallinity and electronic band structure.[1–3] Hg overlayers (*vide infra*) follow the trend reported extensively for the rare-earth elements,[4–10] where high-Z atoms possess considerable anistropy in the charge distribution and also exhibit an electronic density of states that is sensitive to structure. The complication of the metal–insulator transition, with its attendant change in electronic structure, is not observed for mercury adsorbed on surfaces where it adopts the square lattice of the substrate.[11–13]

II. EXPERIMENTAL

Previous reports[1–3,13–17] of the Hg on Ag(100) system have established that Hg overlayers on Ag(100) form ordered overlayers. Since the goal of our investigation is the relationship between overlayer long-range crystallographic order and branching ratio, we have studied four overlayer thicknesses: 0.6, 1, 2, and 5 monolayers (ML). In each case, we measured the integral photoemission intensities from the Hg $5d_{5/2}$ and $5d_{3/2}$ levels, which possess binding energies of 8 and 9.8 eV below the Fermi edge, respectively. The branching ratio were calculated from a given energy distribution curve (EDC) by taking the ratio of the $5d_{5/2}$ signal versus the $5d_{3/2}$. This ratio is then plotted as a function of the incident photon energy. For each coverage we observed a new electronic state[1–3,14,16,17] for ordered overlayers that is absent for disordered overlayers. A coverage of 0.6 ML is the smallest thickness that exhibits the new electronic state. The

new state possesses a binding energy of ~7.2 eV and is included in the $5d_{5/2}$ oscillator strength unless otherwise noted.

The EDC's were obtained using polarized light with the vector potential parallel with the surface. The photoelectrons were collected normal to the surface as described elsewhere.[17]

Long-range order (or lack there of) was ascertained using low-energy electron diffraction. We observe that 1 and 2 ML of Hg continue the Ag(100) fcc structure (bulk Hg is rhombohedral), and 5 ML exhibit a cubic $p(1\times4)$ ordering.[17] All overlayers were free of contamination to the limit of our Auger electron spectroscopy system (1 at. %) and deposited and analyzed as previously described.[14,17]

The experimental apparatus, previously described,[14,17] was modified by adding a cold stage capable of cooling the Ag(100) crystal substrate to 30 K. The Hg overlayers were deposited at substrate temperatures ranging between 30 and 90 K, and subsequently studied over a temperature range of 30 to 200 K. The Hg overlayer melting temperature was experimentally measured as 150 K ($\pm$ 20 K) using a Chromal–Alumel thermocouple. The overlayer thickness was estimated from Auger electron spectroscopy and photoemission data, as described in detail elsewhere.[14,17]

III. RESULTS AND DISCUSSION

As shown in the inset to Fig. 1, following the adsorption of 1 and 2 (well-ordered) ML of Hg on Ag(100) at 90 K, three 5d-like Hg features may be identified.[14,17] For normal emission, these features have binding energies of 9.8, 8.0, and 7.2 eV with respect to the metal Fermi energy. These features are assigned to the Hg $5d_{3/2}$ (9.8 eV), the Hg $5d_{3/2}$ (8.0 eV) orbitals, and a third feature believed to be the result of Hg–Hg orbital interactions (hybridization).[1–3,14,17] The new electronic states, highlighted with an arrow, are not reported
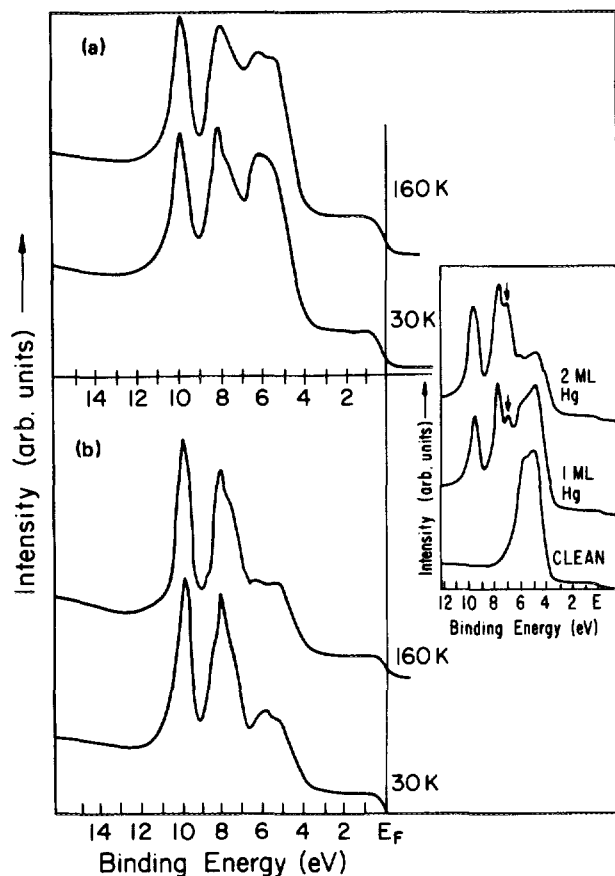
FIG. 1. Angle resolved photoemission spectra for a Hg overlayer deposited on Ag(100) at 87 K (insert), at 30 K, and upon annealing the sample to the thin-film melting temperature (~ 160 K). The spectra were taken for 1 (a) and 2 (b) ML of Hg. The photon energy was 50 eV, and the electrons were collected normal to the surface with the vector potential of the incident light in the plane of the surface in the ⟨110⟩ direction. The third (new) state believed to be a result of Hg–Hg interactions, observed for the ordered thin films, is indicated with an arrow, in the inset.

for gas phase Hg.[18,19] One- and two-monolayer Hg overlayers adsorbed on Ag(100), at 90 K, adopt the fcc (square) lattice of the Ag(100) substrate as evidenced by low-energy electron diffraction (LEED) results discussed elsewhere.[17]

Figure 1 illustrates the angle resolved photoemission spectra taken at normal emission for disordered 1 [Fig. 1(a)] and 2 [Fig. 1(b)] ML Hg overlayers on Ag(100). The Hg was deposited with the substrate temperature at 30 K; the result was the formation of disordered solid Hg overlayers. These overlayers were subsequently and repeatedly annealed at 160 to 200 K and quenched to 30 K with no apparent change in the photoemission spectra taken following the requenching to 30 K. The spectra for the "melted" Hg overlayers annealed at 160 to 200 K are also shown in Fig. 1. The LEED patterns of these Hg overlayers were indicative of a surface with considerable disorder and confirmed the lack of long-range crystallographic order for both the solid (adsorbed at 30 K) and liquid overlayers.

The liquid overlayers exhibit photoemission spectra qualitatively different from well-ordered Hg overlayers. The

electron density of states, in the region of 6 to 7 eV binding energy, between the 5d Hg shallow core levels and the Ag(100) d band (at ~ 5-eV binding energy) increased upon melting with the Ag d-band intensity decreasing. This change is reversible up to ten annealing cycles (the largest number performed), for both 1 and 2 ML of Hg adsorbed on Ag(100).

The Hg overlayers continue to "wet" the surface upon melting. If clumping or island formation (or indeed even alloying) accompanied the melting of the Hg overlayer, then the substrate Ag photoemission signal should increase, not decrease as observed. In addition, the changes in the photoemission features with temperature are reversible, arguing against substantial overlayer structural changes.

When the Hg overlayer is melted, not simply disordered, we expect the Hg atoms to occupy a variety of sites (in contrast to the thermodynamically most stable sites). This causes the broadening of the photoemission features observed, from the Hg overlayer adsorbed at 30 or 90 K, as indicated by the results in Fig. 1. These results demonstrate that the electronic band structure of the disordered and melted overlayers differ and indicate the presence of local crystallographic order in the disordered overlayers.

Several studies of amorphous materials[20] have established that the nearest-neighbor and next-nearest-neighbor spacings and orientations remain predominantly the same for amorphous materials and their crystalline counterparts. Similarly, because Hg atoms adsorbed at 30 K will most likely occupy the most stable sites, which are the same sites occupied by Hg atoms in the ordered overlayer formed with adsorption at 90 K, the principle difference in adsorption of Hg at 90 and 30 K is the long-range crystallographic order of the Hg thin film. Neither the disordered solid Hg overlayer nor the melted Hg overlayer exhibit an electronic density of states containing the same features as those observed in the spectra of the ordered $p(1 \times 1)$ of 1 and 2 ML of Hg formed at 90 K[14,17] (as seen in Fig. 1). The new electronic states (highlighted with an arrow in the inset to Fig. 1) are a consequence of the strained Hg ordered overlayer structure.[2,13,21] There is no observation of similar electronic states in the disordered Hg overlayers adsorbed at 30 K. This implies that long-range order is necessary for such states. Because the disorder of the overlayers formed at 30 K is largely going to be a result of defects, we conclude that short-range crystallographic order is not sufficient for the formation of such new Hg electronic states, since the local geometry about each atom is little different between adsorption at 30 and 90 K.

Judging from the experimental observations of the total density of states, one would expect the electronic density of states, broadly speaking, to remain similar.[22–25] The present results therefore suggest one of two unexpected possibilities: the nearest-neighbor crystallography differs significantly for ordered and amorphous films of Hg, or local density of states models for band structure are not applicable.[22] Indeed, the change in the electron density of states is far greater than expected from even a change in lattice constant[2,21] or the crystallographic symmetry.

Since the photoemission cross section of the Hg core levels

are generally regarded as atomic in origin, the Hg/Ag(100) system is particularly suited to investigate solid-state effects on the cross section in detail. Figure 2 illustrates a direct comparison of a disordered 5 ML Hg overlayer (open circles), a well-ordered 5-ML Hg overlayer (crosses with solid line),[15] and the gas phase results[26,27] (broken lines). These various cross sections in Fig. 2 have been normalized to be equal at 52 eV. This figure demonstrates that the disordered Hg overlayer exhibits a partial cross section quite similar to that observed for gaseous Hg[26-35] and distinct from the partial cross sections attributable to the well-ordered Hg overlayer.[15] The cross section of the disordered overlayers does not appear to be sensitive to the thickness of the Hg overlayer. The partial cross sections, therefore, depend on the long-range crystallographic order. We also note that for the disordered Hg overlayer, there is no indication of the narrow [full width at half-maximum (FWHM) approximately 1 eV] resonance so prominent in the well-ordered Hg overlayer.[15]

While recent theoretical calculations for Hg and Rn suggest that heavy metal partial cross sections of Hg are subject to the *Ef*-wave potential,[36] the cross section has never been demonstrated to depend upon long-range crystallographic order. Since both the sharp (1–2 eV full width at half-maximum) cross-section resonance feature at 59 eV and the broad featured (35–45 eV full width at half-maximum) about 65 eV are altered by the crystallographic order, photoemission diffraction effects *cannot* be used to explain all of our observed cross-section changes. Photoemission diffraction can alter the partial photoemission cross sections[37,38] only at specific photon energies, and result in changes in the cross section only over small (~2 eV) photon energy regions. The necessary conditions[37,38] for such photoelectron diffraction are not satisfied. A change not in the local order, but in the long-range crystallographic order must, therefore, somehow have a profound effect upon the electronic structure of the Hg overlayer.
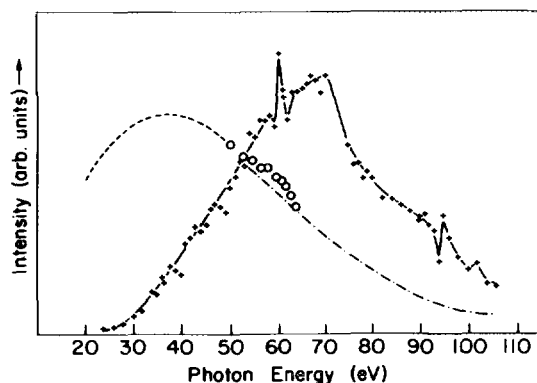
To confirm that defects in the long-range crystallographic order affect the Hg 5d partial cross sections, we deposited 20 L (7 ML) of Hg on Ag(100) held at 70 K and produced a disordered Hg overlayer with no LEED pattern, and with only a weak feature in the photoemission attributable to the third 5d Hg feature. We measured the partial cross sections of the 5d-like states for the photon energy range 50 eV $\leqslant hv \leqslant 60$ eV. We annealed the sample gently (to ~100 K) and cooled the sample back to 70 K after each annealing treatment.

As the overlayer is annealed, the long-range order increases, as demonstrated by LEED, and the partial cross section of the three 5d-like Hg states changes. Since the coverage does not change, the cross-section changes can only be due to changes in the structure. The change in the cross section is precisely the expected: as the defect density is reduced by annealing, and the long-range order increases, the cross section changes from that characteristic of gas phase Hg (decreasing with photon energy) to that of the well-ordered Hg overlayer (increasing with photon energy). The cross section of all three Hg 5d states depends upon long-range crystallographic order of the Hg overlayer.

The 2- and 5-ML overlayers exhibit both well-ordered and disordered overlayers. The new electronic state was present in the photoemission spectra of the well-ordered overlayers and absent for the disordered overlayers. Figure 3 illustrates the branching ratio for well-ordered 2-ML (crosses) and disordered 2-ML overlayers (open circles) obtained by depositing Hg onto a Ag(100) sample held at 90 and 30 K, respectively, in the photon energy range from 50 to 70 eV. Note that the disordered 2-ML overlayers closely resembles the gas phase Hg results.[28,29,39] The well-ordered Hg overlayers exhibit a significantly higher branching ratio by comparison, some 10% to 40% higher than the gas phase results.
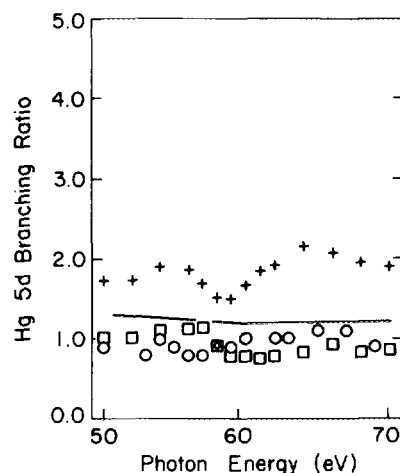

FIG. 2. The relative photoemission cross section of the Hg $5d_{5/2}$-like orbital for a 5 monolayer (13–14 L) thin film of Hg on Ag(100) at 30 (O) and 87 K (+). The relative cross sections were compiled from EDC's taken with the collection angle normal to the surface and the vector potential of the light parallel with the surface. The gaseous mercury cross section is shown as (- - -) from Ref. 26 and (-·-·-) from Ref. 27.

FIG. 3. The branching ratio for the Hg 5d states as a function of photon energy for 2 ML of Hg adsorbed on Ag(100). (+) represents the 5d ratio for an ordered overlayer adsorbed at 90 K and with the third 5d Hg feature included in the ratio, while the (□) symbols indicate the ratio for this overlayer without incorporation of the third feature intensity. (O) indicates the $5d_{5/2}$ to $5d_{3/2}$ ratio for a disordered 2 ML overlayer of Hg on Ag(100) at 30 K. The solid line is the observed branching ratio for gaseous Hg (Refs. 28, 29, and 39).

The branching ratio obtained for the well-ordered and disordered 5-ML Hg overlayers are illustrated in Fig. 4. We observed a dramatic difference between the well-ordered overlayer (crosses) and a disordered Hg overlayer of equal thickness (open circles) as shown in Fig. 4. The well-ordered Hg overlayer exhibits two maxima in the branching ratio, a sharp (FWHM = 4 eV) maximum of 7.2 at a photon energy of 28 eV and a broad maximum of 2.6 at ~68-eV photon energy. The gas phase results ($\triangle$) of Refs. 28, 29, and 39 exhibit corresponding branching ratio of ~1.7 and ~1.4 at photon energies of 28 and 68 eV, respectively. The disordered Hg overlayer exhibits a branching ratio similar to that of gas phase Hg, differing by not more than 15% from the statistical value except at photon energies less than 25 eV. This result, of a comparatively high branching ratio at photon energies below 25 eV, has been previously reported for HgS.[40]

Taking long-range crystallographic order into account in estimating the branching ratio is clearly necessary, as Figs. 3 and 4 demonstrate. The branching ratio of the disordered Hg overlayers resembles the gas phase branching ratio, while the deviation in the branching ratio is clearly apparent when the thin Hg overlayer is ordered. The difference between the two overlayers must lie in the presence or absence of long-range crystallographic order.

Photoemission diffraction can alter the partial photoemission cross sections[37,38] and as a consequence can alter the branching ratio, but such effects, as mentioned previously, can be excluded. It is also worth noting that the large deviations of the branching ratio from the statistical value of 1.5 observed at 28 and 58 eV not only cover too broad a photon energy range to be explained by photoelectron diffraction, but do not correspond to features in the partial cross sections characteristic of photoelectron diffraction (Fig. 2).

The presence of the new electronic state demonstrably and significantly affects the branching ratio. When the influence of the new electronic state is removed either by our data analysis software or by growing disordered overlayers, the branching ratio more closely approaches that observed for gaseous Hg. An understanding of the origin of the new third $5d$ Hg state appears essential to developing any understand-

ing of the observed large deviations of the branching ratio for the ordered Hg overlayers from those branching ratios observed with gaseous Hg and disordered overlayers. There is little doubt that this feature is a consequence of the electronic structure of the Hg overlayer.[17] Furthermore, this third feature is not a result of the electronic structure of the Ag(100) substrate since the feature does not attenuate in intensity with increasing overlayer thickness,[14,17] is observed for Hg overlayers on other metal substrates,[1,16] and cannot be reconciled with the electronic structure of the Ag(100) substrate.[17] The decrease of the partial $5d_{3/2}$ and $5d_{5/2}$ cross sections (neglecting the new state) in the transition from disordered to ordered Hg overlayers suggests that the new $5d$ state is made of approximately one electron from the $5d_{3/2}$ state and one electron from the $5d_{5/2}$ state. The apparent contributions of the $5d_{5/2}$ and $5d_{3/2}$ states to the new Hg $5d$ state oscillator strength are consistent with the general deviation of the branching ratios, observed for the ordered 5- and 2-ML Hg overlayers, of 2.3 as compared to the more statistical value of 1.5 approximated by the disordered overlayers and gaseous Hg. Such a shift in oscillator strength is not consistent with "standard" bonding–antibonding molecular-orbital-type models of hybridization. Such a shift in electron distribution is suggestive of a change in the spin–orbit interaction.

Changes in the spin-orbit interaction can result in substantial changes in the $5d$ branching ratio.[41] Unfortunately, changes in the $5d_{5/2}$ to $5d_{3/2}$ spin–orbit binding-energy splitting expected with a change in the spin–orbit interaction[41] are not observed.[1,2,16] Furthermore, there is no reason to expect a large change in the electron occupancy of $5d$ states 7–10 eV below the Fermi energy, particularly when this change must be greater than is observed for a compound such as HgS,[40] nor is it clear why the spin–orbit interactions (a largely intra-atomic interaction) should be affected by long-range crystallographic order (indicating an extra-atomic many-electron interaction).

The overall Hg $5d_{5/2}$ and $5d_{3/2}$ partial cross sections for well ordered Hg overlayers have the cross-section maximum shifted to higher photon energies and the cross-section maximum is broader than is the case for gaseous Hg.[22,23] Existing calculations,[42] although only considering the nearest-neighbor interactions, have indicated that such a shift in the broad maximum in the photoemission cross section is consistent with a change in the exchange-correlation potential for the interaction between a given atomic orbital and the surrounding atoms, from a localized one-electron, self-consistent-field potential to a potential accommodating essentially free-electron states. In the example reported here, for the well-ordered Hg overlayers, the Hg $5d$ levels appear to interact in a manner consistent with a many-electron exchange and correlation potential. Noting that the cross section of the $5d$ Hg levels depends upon long-range crystallographic order of the overlayer, the implication is that the Hg $5d$ interaction extends beyond the second nearest neighbor.
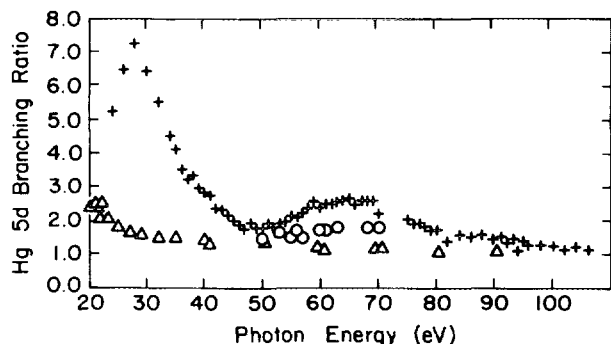

FIG. 4. The branching ratios of the Hg $5d$ states for a 5-ML-thick overlayer of Hg on Ag(100) as a function of photon energy. (+) shows the ratio for an ordered overlayer and the third-feature intensity included in the ratio. ($\triangle$) shows the ratio for gaseous monoatomic Hg (Refs. 28, 29, and 39). (O) shows the results for a disordered overlayer.

IV. CONCLUSION

In summary, we have observed three types of qualitative changes in the photoemission cross section of well-ordered

Hg overlayers on Ag(100) as compared to gas phase Hg and have established the essential role of *long-range* crystallographic order upon the electronic stucture, a heretofore unreported relationship. Long-range order affecting the electronic structure of semiconductors has been postulated[43] but without the clear evidence presented here. We have also demonstrated the necessity for long-range crystallographic order for observing the new Hg overlayer electronic states. The change in the density of states is a dramatic change, and cannot be explained by a simple broadening of the local density of states. We have thus established that the presence or absence of long-range crystallographic order influences the photoemission cross section of Hg electronic states 8 and 10 eV below the Fermi energy, commonly viewed as shallow core levels.

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