Surface Resonance on W(100): Effects of Au and Cu Adsorption

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Measurements of energy-resolved field emission from W(100) show that the surface resonance can exist even in the presence of adsorbed Au and Cu. A cyclical pattern is seen in which the resonance exists only at 0, 1, and 2 monolayers of coverage. A model relating these results to the symmetry of the top partial layer is proposed.

Using the extremely surface-sensitive method of field-electron energy distribution measurement (FEED) we have recently observed surprising new effects of gold and copper adsorbate layers on the surface density of states (SDOS) of W(100). We propose a model which relates these pheonomena primarily to the surface symmetry of the adsorbate atoms. This interpretation could have substantial impact on theoretical ideas about surface density of states, surface states/resonances, and adsorbate ordering.

Controversy has long existed over the origin of the anomalous field-emission peak observed at 0.4 eV below the Fermi energy on W(100).[1] It is believed to be a surface resonance existing in a symmetry-induced energy gap but details of its theoretical characterization are disputed.[2] Recent calculations of the emission from this state have been made by Nicolaou and Modinos[3] and by Weng[4] although both these works yield incorrect dispersion effects. A self-consistent calculation by Kerker, Ho, and Cohen[5] should correctly describe the similar state for molybdenum but relativistic effects, necessary for tungsten, have not been treated. No theoretical calculation has been able to reproduce quantitatively the amplitudes of measured spectra and relatively small features such as the d-band structure observed on clean surfaces are seldom even considered.

Adsorption phenomena have played a major role in the study of W(100). Carbon monoxide and other molecular adsorbates rapidly quench the anomalous peak.[6] Similar quenching by xenon and krypton[7] has been seen as indicative of a surface state.[2] Given the long-recognized fact that all adsorbates suppress the surface state, several recent experimental results are quite surprising. Photoemission from a W(100) crystal has shown the 0.4-eV peak through a saturation coverage of mercury.[8] Richter and Gomer[9] deposited gold on a field emitter and observed the resonance to diminish slowly with coverage before vanishing suddenly at just over one monolayer. The present work has found a different gold behavior which supports the surface-resonance proposal and adds copper to the list of such adsorbates.

The experimental equipment has been previously described[10] and the procedures and data treatments are all standard and well reviewed.[2] Work functions were determined by the Fowler-Nordheim method as shifts from the clean-tungsten value. Enhancement factors are simply the measured energy distributions divided by an appropriately calculated free-electron distribution. This removes the dominating exponential character of field emission so that structure in the curves is more clearly revealed.

Figure 1 shows the measured work-function changes for coverages of gold and copper on W(100) along with similar results from the literature.[9,11] Our curve for gold has a reproducible, previously unobserved dip at one-half monolayer. Such work-function curve shapes are quite common and are usually associated with charge-transfer and depolarization effects.[12] There is no complete explanation why the work-function minimum tends to occur at or about half-monolayer coverage. Occurrence of the $c(2\times 2)$ surface structure at the same coverage probably has no direct correlation with the work-function minimum other than the obvious consideration that both effects are associated with adsorbate interactions which take place at about $\theta \simeq 0.5$. Similar inflections have always been seen with copper but fall at something over a full monolayer. This is particularly significant here because our interpretation of the energy distributions strongly suggests that both minima are actually at one-half monolayer.

It is possible that diffusion has greatly altered the local adsorbate densities. Large effective sources and/or sinks of atoms exist in the regions closely surrounding an observed plane on a field emitter, and initial atom mobility is implied by our model. Evidence exists that copper completely diffuses off the W(100) plane at

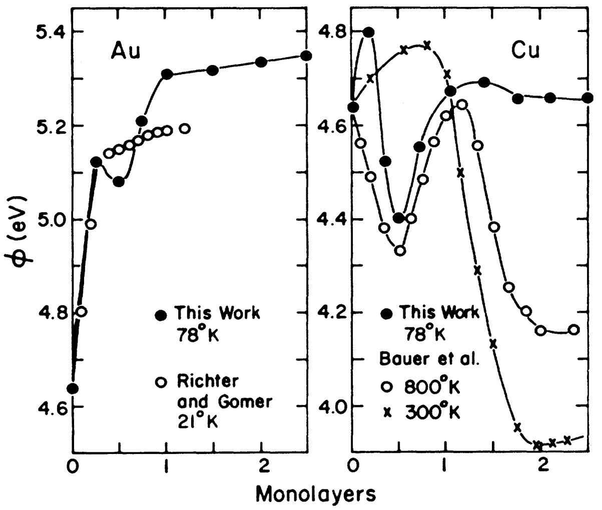


FIG. 1. Work-function changes with gold and copper coverage.

600 K.[13] The work-function curve for 800 K on a macroscopic crystal has a minimum at one-half monolayer which is associated with an ordered $c(2\times 2)$ LEED pattern.[11] We believe that ordering occurs on our emitter tips even at low temperatures and suggest that a combination of the 300- and 800-K macroscopic curves applies including an initial rise and a minimum at one-half monolayer. In the following discussion quoted copper coverages have been adjusted to fit this interpretation.

Figure 2(a) shows typical enhancement factors for gold on W(100). There is no significant change if the emitter temperature is varied from 78 to 430 K during deposition. Two very important points must be noted from Fig. 2(a). First, the clean spectrum, including the surface resonance, is almost exactly reproduced with gold coverages of one and again of two monolayers. Second, the spectra in between integral monolayers, labeled B, C, and D, are seen to form a cyclically repetitive series of characteristic spectral shapes. The shapes are not understood but their repetitive nature is significant.

Copper is sensitive to temperature changes. Data for 78 K are plotted in Fig. 2(b). A substantial correlation exists between these curves and those for gold. The one- and two-monolayer coverages again contain a structure which appears to be the tungsten surface resonance. The major difference between gold and copper is that the latter enhances the energy region around 0.8 eV.

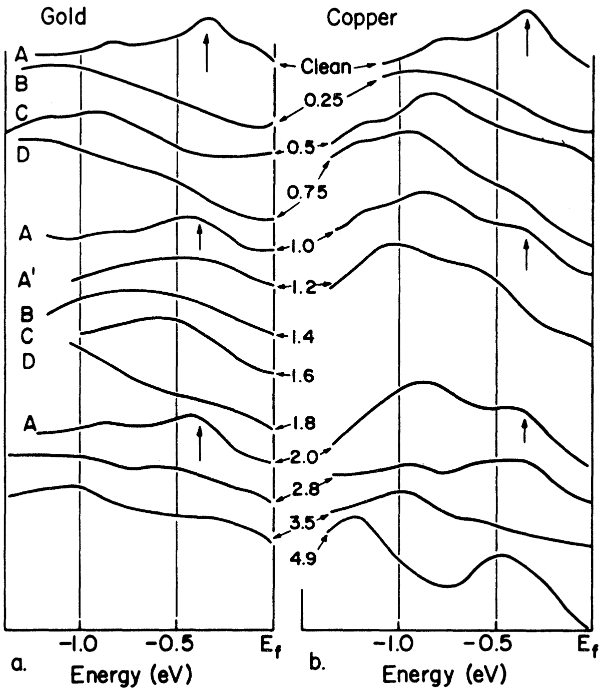


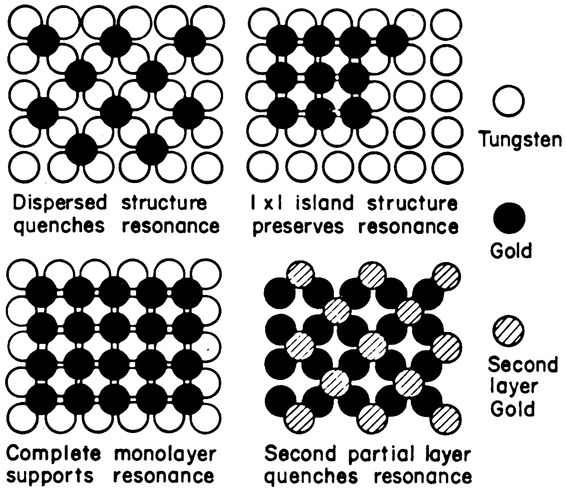
FIG. 2. Enhancement-factor spectral changes with gold and copper coverage.

We now outline a model which explains a large amount of experimental data with considerable consistency. It is based on an approach by Kar and Soven,[14] who performed a numerical calculation for field emission from W(100) through two different types of adsorbate layers. Replacing tungsten pseudopotentials by potentials for gold in the last atomic layer did not quench the resonance. With xenon potentials in a typical $c(2\times 2)$ overlayer structure the resonance disappeared.

Since the calculation of Kar and Soven[14] is a direct extension of the Nicolaou and Modinos[3] method, their numerical results are also of questionable validity. Kar and Soven, however, made the following significant qualitative hypothesis.[14] They suggested that the critical factor determining the presence of the surface resonance is the symmetry of the adsorbate layer. The atomic potentials (i.e., the chemical composition of the overlayer) are of secondary importance. Any of several metals is apparently satisfactory. They predicted that as long as the overlayer has (1×1) symmetry [i.e., the adsorbed atoms are in W(100) sites] the resonance should persist. Lower symmetries cause degeneracies and provide new decay paths which can broaden and quench the resonance. Without making any claims about the validity of their calculational method we suggest that this symmetry argument is precisely correct.

Figure 3 illustrates the structural sequence that we believe occurs. We assume a repulsive adsorbate-adsorbate interaction[11] and, in our experiments, sufficient activation energy for the adsorbed atoms to assume their preferred dispersed sites. On the small field-emitter crystal plane this would be functionally equivalent to the adsorbate ordering on macroscopic crystals at 600 to 800 K.[11] At submonolayer coverages the (1×1) symmetry is destroyed and so the W(100) resonance is quenched. Our smallest dose, 0.25 monolayer, completely removed the clean-tungsten structure. The W-Au bond is stronger than the Au-Au bond,[15] and gold is known for its ability to form smooth overlayers so that a perfect pseudomorphic monolayer should result at a coverage of $1.0\times 10^{15}/\text{cm}^2$. Now the resonance does not decay; it propagates through the gold layer essentially unattenuated.

Surprisingly, the second gold layer behaves in a manner identical to the first. The resonance vanishes just above 1.0 monolayer and the same sequence of spectra are observed until the resonance returns at 2.0 monolayers. We conclude that nearly all the emission comes from the top partial monolayer, that its structure and symmetry are decisive, and that as long as the gold remains in a tungsten-type crystal structure it does not matter whether the atoms are tungsten or gold. Apparently the SDOS on top of two pseudomorphic layers of gold is essentially the same as for a clean tungsten surface. Our data for very high coverages are not conclusive but we have not seen the resonance at 3.0 layers.



Dispersed structure quenches resonance

I x I island structure preserves resonance

Complete monolayer supports resonance

Second partial layer quenches resonance

FIG. 3. Model for surface structure of deposits.

If the resonance only exists with a (1×1) surface layer and Richter and Gomer[9] observe it at all submonolayer coverages, one must postulate that their experimental conditions caused growth of the (1×1) islands also indicated in the work with mercury.[16] Thus (1×1) gold and (1×1) tungsten are continuously present and the resonance never vanishes. Richter has recently suggested exactly this explanation for their results.[17] The experimental conditions causing different ordering kinetics between our work and theirs are not clearly defined. Known factors include different substrate structures (field evaporated versus annealed) and somewhat different thermal conditions. Defects on an annealed tip may act as nucleation sites for island growth, while an absence of defects coupled with greater kinetic energy gives more dispersed ordering. The diffusion barrier is much lower for a second gold layer[11] consistent with Richter and Gomer's observed loss of the resonance at slightly above a monolayer. We would expect the resonance to return again at two layers had their experiment continued.

We have found that copper constitutes a third material (after mercury and gold) which can support the tungsten resonance. Although these three metals are similar they do enhance the belief that the atomic potential of the surface atoms is not particularly critical. As with gold, the resonance vanishes initially and returns at integral monolayers. The difference is that copper enhances energies around 0.8 eV. At elevated temperatures copper grows a fcc crystal and displays a very large peak at 0.8 eV.[13] This probably represents a copper surface state but space prevents its discussion in this Letter. Presumably copper still has some predisposition towards states of this energy even when it has the wrong crystal structure. An effect similar to the resonance tunneling enhancement phenomenon predicted[18] and observed[19] for atomic adsorbates may be occurring. However, we see a collective effect of the copper layer instead of an atomic energy state. The small 0.8-eV peak in the clean-tungsten spectrum may play a role in exciting the resonance since it is seldom found for copper on other crystal planes and substrate materials.

While our discussion has been stated in terms of the W(100) surface resonance, we wish to point out that in fact other characteristics of the (100) clean spectrum (the 0.8-eV peak and the general spectrum shape) vanish and return in precisely the same manner. The effect of overlayer symmetry on the surface density of states appears to be more significant that previously assumed. The Kar-Soven hypothesis implies that this could occur but the extent to which the band structure mixing and consequent SDOS scrambling apparently proceeds is surprising.

To summarize briefly, we find that the atomic ordering and crystal structure of gold and copper overlayers on tungsten is the primary factor determining the SDOS. Both metals can effectively mimic tungsten even with two adsorbed monolayers. With integral monolayers of gold the measured energy spectra are essentially undistinguishable from those for clean tungsten. The proposed condition is simply that the overlayer atoms assume a (1 × 1) pseudomorphic order. Considerable practical complication and interpretive richness is present, however, since the kinetic mechanisms of ordering are very sensitive to experimental conditions. Changes of substrate temperature and crystal orientation, among others, are sufficient to cause effects such as the switch from a (1 × 1) island adsorbate growth to a dispersed low-density structure. Although ordering behavior is the main consideration, electronic effects such as the ability of copper to form a surface state, thus enhancing one part of the spectrum, must also be considered.

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Light Scattering as a Probe of Dynamical Critical Properties of Antiferromagnets

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It is shown that well-known coupling of electric fields to pairs of spin operators leads to the possibility of studying certain response functions of interest in critical phenomena by means of inelastic–light-scattering experiments.

Light-scattering experiments have been widely used to study dynamical critica phenomena in liquids.[1] In magnetic materials, however, inelastic–neutron-scattering experiments have been more often employed,[2] partly because light does not always couple in a simple way to the magnetization (or staggered magnetization) of a magnet (or antiferromagnet). It would be useful in improving understanding of the dynamics of critical phenomena in antiferromagnets to be able to more readily use light-scattering