for the first time and the r^{-2} shielding behavior in Ge. A more detailed version of the theory is in preparation.

Helpful discussions with Farrell Lytle and comments by Jesse Sabo are gratefully acknowledged.

*Research sponsored by the U. S. Air Force Office of Scientific Research, Air Force Systems Command, under Grant No. AFOSR-71-1967B.

†Research supported in part by the Advanced Research Projects Agency of the Department of Defense and monitored by the U. S. Army Research Office (Durham) under Contract No. DAHC04-71-C0010.

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Photoemission Observations of Resonant *d* Levels and *d*-Band Formation for Very Thin Overlayers of Cu and Pd on Ag†

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(Received 17 August 1972)

Photoemission studies of very thin overlayers of Cu and Pd on Ag substrates show resonant bound *d* states with half-widths $\Gamma \simeq 0.5$, and 0.8 eV centered at 2.5 and 1.2 eV below the Fermi energy E_F, respectively, for depositions $\lesssim 2$ average monolayers, and show the formation of bulk band structure for deposition $\gtrsim 4$ monolayers. The *d*-resonance position for Pd on Ag (1.2 eV below E_F) is markedly different from that of dilute Pd in AgPd alloys (2 eV below E_F), while the level widths are comparable.

We report photoemission measurements of electronic energy level positions and level widths for very thin overlayers of Cu and Pd deposited on Ag substrates, Recently, there have been a number of spectroscopic measurements of adsorbates on metal surfaces. These include field-emission spectroscopy (FES) studies of alkaline-earth adsorbates on tungsten,[1] for which the ionization potential of the adsorbate I^{ads} is less than that of the substrate (i.e., $I^{ads} < I^{sub}$) and electrons tend to be transferred to the substrate, and ion neutralization spectroscopy (INS) and photoemission electron spectroscopy (PES) studies of chalcogen adsorbates[2] and gaseous adsorbates (O, CO, etc.) on metal surfaces,[3-5] for which $I^{ads} > I^{sub}$ and electrons tend to be transferred to the adsorbate.

In this work, we have essentially neutral adsorption ($I^{ads} \simeq I^{sub}$), and for average adsorbate coverages of $\lesssim 1$ monolayer we observe the relatively simple situation in which the adsorbate *d*-state resonances for Cu and Pd lie above the *d* bands of the Ag substrate and are degenerate with the Ag "*s*" bands. For Cu and Pd, respectively, we observe occupied resonant bound state *d* levels of half-width $\Gamma \simeq 0.5 - 0.8$ eV centered at about 2.5 and 1.2 eV below the Fermi level E_F. Our observed level widths appear to be consistent with the Anderson model as applied to chemisorption,[6,7] and are similar to observed level widths for dilute Pd in AgPd alloys.[8,9] Quantitatively, a recent Korringa, Kohn, and Rostoker (KKR) calculation by Cooper[10] for a 1-monolayer film of Cu embedded in a simple metal predicts a Cu *d* state of half-width $\Gamma \simeq 0.50$ eV centered at -2.7 eV.

As the adsorbate deposition was increased from about 1 to 4 average monolayers for Cu and Pd (the deposited mass was monitored), the adsorbate energy distributions were observed to change in shape from asymmetric Lorentzian-like shapes to shapes characteristic of the bulk metal. Also, adsorbate-induced emission characteristic of nondirect optical transitions is observed for de-

positions of less than about two average monolayers, while emission characteristic of direct momentum-conserving transitions is observed for the bulk.

Photoemission energy distributions and quantum yields were measured for photon energies $5 \leq h\nu \leq 11.6$ eV using a 1-m normal-incidence monochromator with a hot-filament Hinterregger-type H_2 gas-discharge lamp and an energy analyzer consisting of the emitter (~2 cm^2 area) and a 4.5-cm-diam spherical retarding collector. Specimens were prepared *in situ* near room temperature by evaporation onto clean Ag substrates using W-filament evaporators for Cu and Ag and an electron-beam-gun evaporator for Pd. Average film depositions were determined by measuring their mass using two 4.1-MHz quartz-oscillator rate monitors and evaporation rates were typically about 0.2 monolayers/sec. Depositions of Cu and Pd are quoted in terms of the average number of monolayers $\bar{n}$, assuming bulk densities, and appear to be quasicontinuous overlayers.[11] Base pressures of $\sim 5\times10^{-11}$ Torr were typically reached, with operating pressures during evaporation in the low to mid 10^{-9} Torr range which then rapidly fell to $\lesssim 5\times10^{-10}$ Torr within 30 sec after completion of the evaporation.

The experimental technique and sensitivity are illustrated in Fig. 1, which shows energy distribution curves (EDC's) at $h\nu = 8.6$ eV for a Ag substrate and for Ag with an average coverage of $\bar{n} = 1.1$ monolayers of Cu. Extra emission associated with the Cu adsorbate is shown [Cu($\bar{n} = 1.1$)] and exhibits an asymmetric d-state resonance with a peak at -2.4 eV (i.e., 2.4 eV below the Fermi level E_F) and a half-width $\Gamma \simeq 0.5$ eV, as well as broad emission between E_F and -2 eV, which presumably is associated with the Cu s levels. The sharp peak at -4 eV in Fig. 1 corresponds to emission from the top of the Ag d bands. Figure 1 also illustrates our technique for determining emission associated with the adsorbate. EDC's for various adsorbate/substrate specimens are first normalized to their quantum yield (i.e., emitted electrons per incident photon). We observe that the spectral shape of the substrate d-band emission does not change with adsorbate coverage and assume that the entire Ag spectral shape does not change, i.e., only its amplitude diminishes with increasing adsorbate coverage. Then, EDC's at $h\nu = 10.2$ eV (arbitrarily chosen) for pure Ag are scaled down in amplitude so as to have the same Ag d-band amplitude at -4 eV as observed for the composite adsorbate/Ag specimen and are subtracted from the normalized composite EDC's.[12] For each deposition $\bar{n}$ this scale factor was used for both $h\nu = 10.2$ and 8.6 eV. Also, corrections for work-function changes with absorbate coverage are included.[12]

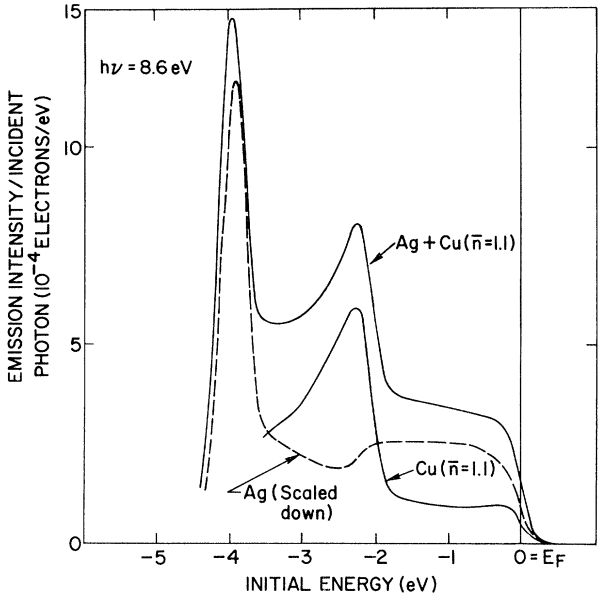

FIG. 1. Energy distribution curves for bulk Ag (dashed) and for Ag + 1.1 average monolayers ($\bar{n}$) of Cu ($\bar{n}$ is based on the deposited mass, assuming the bulk Cu density) are shown as well as the difference curve (lower solid curve) which shows emission due to the adsorbed Cu alone.

EDC's for the extra emission of very thin overlayers of Cu on Ag are shown in Fig. 2 for several depositions, together with an EDC for bulk Cu. The Ag "background" emission was subtracted according to the above-mentioned prescription. For the lower average coverages, $\bar{n} = 0.4$ and 1.1 monolayers in Fig. 2, we observe an asymmetric Cu d-state level with a peak at -2.4 eV and half-width $\Gamma \simeq 0.5$ eV. The asymmetry in the line shape, i.e., increased emission on the low-energy side, might be due in part to inelastic scattering processes and might also be due in part to an antiresonance effect as described by Penn.[13] A widely used approach to the chemisorption problem is the Anderson model,[6,7] for which the level width 2Γ is given by Fermi's "golden rule" as $2\Gamma = 2\pi |V_{sd}|_{av}^2 \rho(E)$, where $\rho(E)$ is the substrate s-band density of states at the resonant energy and $|V_{sd}|_{av}$ is the phenomenological s-d hopping integral. Assuming the bulk value $\rho(E) \approx 0.26$ electron/eV atom

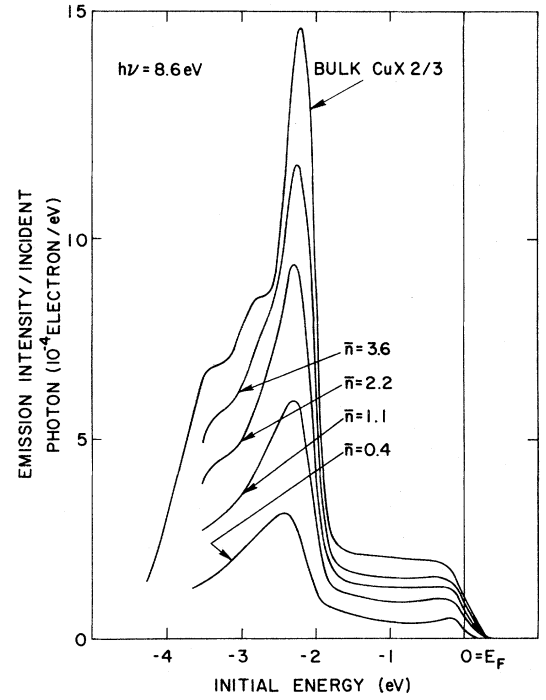

FIG. 2. Extra emission due to Cu overlayers of 0.4 to 3.6 average monolayers, as well as the bulk Cu emission. Deposition values $\bar{n}$ are estimated to be accurate to ±30%.

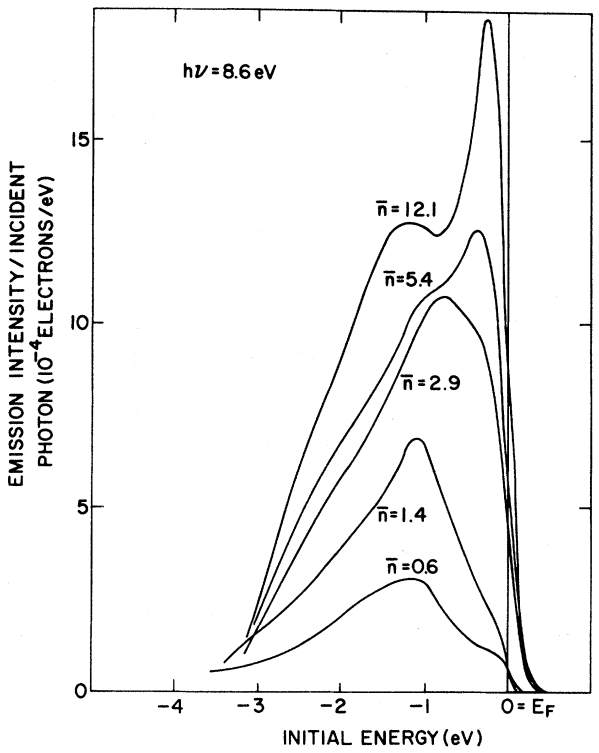

FIG. 3. Extra emission due to Pd overlayers of 0.6 to 12.1 average monolayers of Pd on Ag.

for Ag, we obtain $|V_{sd}|_{av} \approx 0.78$ eV for Cu on Ag, in qualitative agreement with estimates for resonant bound d states in dilute alloys.[6] Recently, Cooper[10] has calculated the band structure of a monolayer film of Cu sandwiched between two thicker layers of a simple metal using the KKR Green's function method. Using the Chodorow potential for Cu, he has obtained a Cu d band of half-width $\Gamma \simeq 0.5$ eV centered at -2.7 eV below E_F.[10] His calculations of both level width (which was determined to be relatively insensitive to boundary conditions) and level position are in good agreement with our measurements. However, caution must be used in making this comparison of level positions since they are expected to be influenced by the different boundary conditions in his calculation and our experiment. Also, Ag is not a simple metal, i.e., its d bands could influence the Cu d-peak position and width.

In Fig. 2, as the Cu coverage is increased from $\bar{n} = 1.1$ to 3.6 average monolayers, peak structure characteristic of bulk Cu is seen to develop. That is, the peak at -2.4 eV for the lower coverages shifts ~0.2 eV towards E_F and gets much sharper, and two shoulders in the EDC appear at -2.8 and -3.2 eV, just as is seen for bulk Cu. The structure seen for bulk Cu changes with photon energy and is due to direct momentum-conserving optical excitations. In contrast, the Cu-induced emission for coverages $\bar{n} \leq 2$ does not change shape with photon energy. That is, the adsorbate emission for small $\bar{n}$ appears to be due to nondirect optical excitations, as is expected because of the lack of the bulk crystalline periodicity.

EDC's for the extra emission of very thin overlayers of Pd on Ag are shown in Fig. 3 for depositions ranging from $\bar{n} = 0.6$ to 12.1 average monolayers. For the lower average depositions $\bar{n} = 0.6$ and 1.4, we observe a Pd d-state level centered at about -1.2 eV with a half-width $\Gamma_{obs} \simeq 0.8$ eV. The upper edge of this resonant level is cut off by E_F, implying the existence of d-state holes.[8] As the Pd deposition is increased from $\bar{n} = 1.4$ to 5.4 monolayers, we observe large changes in the spectral shape of the EDC's with a rapid buildup of emission from states near E_F. A sharp peak appears at -0.3 eV for $\bar{n}$ between 3 and 5 average monolayers. The EDC for $\bar{n} = 5.4$ is similar to that of "bulk" Pd as depicted by the EDC for $\bar{n} = 12.1$, thus indicating that we are observing essentially bulk Pd for depositions

of $\bar{n} \gtrsim 5$ average monolayers.

A comparison with photoemission and optical studies of bulk AgPd alloys show similar Pd level widths but quite different energy positions (i.e., -1.2 eV for our overlayers with $\bar{n} \leq 2$ versus -2 eV for $\lesssim 20\%$ Pd in bulk AgPd alloys).[8,9] Our observed level half-width $\Gamma \simeq 0.8$ eV for Pd is likely to be broadened by spin-orbit splitting (~ 0.5 eV for the atom), as discussed by Norris and Meyers.[8]

For the two systems we have described, the overlayer d-state resonance for low depositions ($\bar{n} \simeq 2$) lies higher in energy, i.e., nearer E_F, than the center of the corresponding d-band resonance for the bulk metal. Namely, for bulk Cu, the d-band resonance is centered at about -3.6 eV,[14] while Cu ($\bar{n} < 2$) on Ag shows a level centered at about -2.5 eV. For bulk Pd, the d bands are centered at about -2.2 eV,[14] while Pd ($\bar{n} \lesssim 2$) on Ag shows a level centered at about -1.2 eV.

We thank J. Donelon whose technical assistance with the measurements in this paper is greatly appreciated, and G. Padilla, who performed some of the data analysis.

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†Work supported in part by the U. S. Air Force Office of Scientific Research under Contract No. F44620-70-0089.

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[11]The surface structure of our very thin overlayer specimens is unknown, i.e., some islanding might be occurring. However, there are several indications that significant thickness nonuniformity is not occurring. First, electron microscopy studies of very thin overlayers of related systems indicate that quasicontinuous films of Pd and Ni and Ag should exist for very thin overlayers, i.e., $\bar{n} \gtrsim 2-4$ average layers [J. W. Matthews, private communication; see also J. W. Matthews and J. L. Crawford, Thin Solid Films 5, 187 (1970); J. W. Matthews and W. A. Jesser, Acta Met. 15, 595 (1967)]. Second, our set of photoemission data itself is inconsistent with severe nonuniformity, e.g., islanding, since bulklike properties would then be observed for the lower depositions. Third, photoemission studies of hot-electron scattering as a function of overlayer thickness are also consistent with quasicontinuous overlayers.

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