

## Low-energy-electron probing depths in metals

X. Zhang, H. Hsu, F. B. Dunning, and G. K. Walters

*Department of Physics and the Rice Quantum Institute, Rice University, Houston, Texas 77251*

(Received 23 April 1991; revised manuscript received 31 May 1991)

Thin-film techniques are used in conjunction with spin-polarized electron-energy-loss spectroscopy to measure directly the probing depth of low-energy ( $\sim 30$  eV) electrons in metals. The data indicate the probing depth in molybdenum is small ( $\sim 1$  monolayer) but that it is significantly higher for copper ( $\sim 3$  monolayers). These differences are consistent with a model in which inelastic scattering is attributed to electron-hole pair excitation. Effects are also observed that might be interpreted in terms of scattering at the interface between substrate and overlayer.

Spin-polarized-electron spectroscopies provide very powerful probes of the electronic and magnetic properties of surfaces and thin films.<sup>1</sup> Here we report the results of a study of electron probing depths at metal surfaces and thin films using spin-polarized electron-energy-loss spectroscopy (SPEELS). In SPEELS a monoenergetic beam of polarized electrons is directed at the target surface and the polarization of scattered electrons is measured as a function of inelastic energy loss. Spin-flip inelastic scattering results when an incident electron falls into an unoccupied state above the Fermi level with the energy released being transferred to an electron of opposite spin in an occupied state below the Fermi level; the latter electron is ejected from the surface.<sup>2,3</sup> For ferromagnetic materials such creation of an electron-hole pair of opposite spin is termed Stoner excitation.<sup>4-8</sup> Recent SPEELS studies in this laboratory demonstrate that such spin-flip scattering events in paramagnetic materials manifest themselves in scattered-electron-polarization spectra that are characteristic of the target electronic structure,<sup>2,3</sup> as will be discussed further below. Specifically, SPEELS studies of Mo(110) revealed a prominent polarization-loss feature, centered at an inelastic energy loss of  $\sim 5$  eV, while no significant polarization loss over that energy range was observed from Cu(100). This very different behavior provides a means to distinguish between electron scattering from copper and molybdenum; electrons that scatter inelastically from copper do so with very little loss of polarization, whereas those that scatter from molybdenum have a readily identifiable polarization-loss signature. Here we take advantage of this difference to measure directly the probing depth of low-energy electrons in copper and molybdenum by depositing thin molybdenum (copper) overlayers on a Cu(100) [Mo(110)] substrate and observing the appearance (disappearance) of the molybdenum polarization-loss feature. The probing depth is defined here as the thickness of the near-surface region from which  $(1 - e^{-1})$ , i.e.,  $\sim 63\%$ , of the detected inelastically scattered electrons originate. The data indicate that the probing depth in molybdenum is small,  $\sim 1$  monolayer. The probing depth in copper is found to be significantly larger,  $\sim 3$  monolayers. Effects are also observed that are attributed to scattering at the interface between the substrate and overlayer.

The present apparatus is shown schematically in Fig. 1

and has been described in detail elsewhere.<sup>2,3,9</sup> Briefly, a collimated beam of spin-polarized electrons is directed at the target surface and the polarization of electrons scattered inelastically from the surface is measured as a function of energy and angle using a movable retarding-potential Mott polarimeter that is equipped with a hemispherical energy analyzer. The polarized electron beam is produced by photoemission from a cesiated GaAs surface using circularly polarized radiation from a  $\text{Ga}_{1-x}\text{Al}_x\text{As}$  laser. The photoelectrons, which are initially longitudinally polarized, are accelerated and directed through a  $90^\circ$  electrostatic deflector. The emergent beam, now transversely polarized, passes through a series of electrostatic lenses and is then focused on the target surface at an angle of incidence  $\theta_i$ . The polarization  $P_i$  of the beam is  $\sim 0.26$  and can be simply reversed,  $P_i \rightarrow -P_i$ , by changing the sense of circular polarization of the radiation incident on the GaAs photocathode.

Electrons leaving the target surface in a narrow range of angles ( $\sim \pm 5^\circ$ ) about some angle  $\theta_s$  to the surface normal enter a hemispherical energy analyzer that has an energy resolution of  $\sim 0.3$  eV. The polarization of the in-

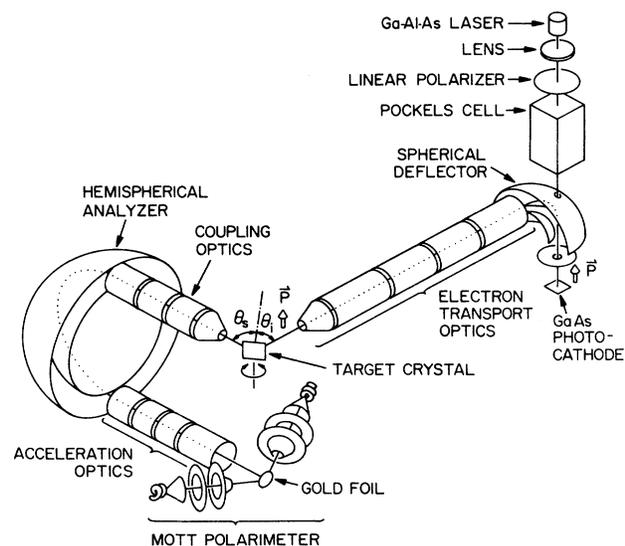


FIG. 1. Schematic diagram of the apparatus is shown.

cident electrons is perpendicular to the scattering plane defined by the incident and scattered electrons. Those electrons transmitted through the hemispherical energy analyzer enter a low-energy Mott analyzer<sup>10</sup> where the average component of their spin polarization perpendicular to the scattering plane is determined by measuring the left-right asymmetry that results because of the spin-orbit effect when the electrons are quasielastically scattered (at 18 keV) through  $\pm 120^\circ$  at a gold surface. In practice, to eliminate instrumental asymmetries, the scattering asymmetry is determined with the incident electrons polarized both spin up and spin down. Ancillary measurements showed that for all the surfaces studied in the present work the scattered-electron currents were essentially independent of the spin of the incident electrons and that any polarization of the scattered electrons produced by an unpolarized incident beam was unobservably small. These observations indicate that spin-orbit effects do not play an important role in determining the polarization of the scattered electrons. It is therefore reasonable to assume that the polarization of the scattered electrons is simply proportional to the polarization  $P_i$  of the incident electrons and will reverse sign when  $P_i$  is reversed. In this event, the polarization of the scattered electrons is given by<sup>2,9,10</sup>

$$P = \frac{1}{S_{\text{eff}}} \frac{X-1}{X+1}, \quad (1)$$

where  $S_{\text{eff}}$  is the magnitude of the effective Sherman function and  $X = (R_L R_R / R_R R_L')^{1/2}$ .  $R_L$  ( $R_L'$ ) and  $R_R$  ( $R_R'$ ) are the count rates in the two detection channels, labeled left and right, with incident-beam polarization  $P_i$  ( $-P_i$ ).

The Mo(110) substrate was prepared by prolonged heating to 1300 K in  $5 \times 10^{-7}$  torr  $O_2$  followed by flashing to above 2000 K. The Cu(100) substrate was prepared by repeated cycles of  $Ar^+$  ion sputtering and thermal annealing to 900 K. Surface cleanliness and order were monitored by Auger-electron spectroscopy (AES) and low-energy electron diffraction (LEED). The copper and molybdenum films were evaporated (with the substrate at room temperature) using thermal and electron-bombardment evaporators, respectively. The pressure in the vacuum system remained below  $\sim 3 \times 10^{-10}$  torr during evaporation and the deposition rates, monitored by a quartz thin-film-thickness monitor, were typically  $\sim 0.2$ – $1.0$  Å per minute. The deposition rates and film thicknesses were determined both by measuring directly the ratio of the copper and molybdenum Auger signals and by monitoring the time development of the Auger features during deposition. Significant breaks in the time development were observed. If, as in general practice, these are taken to signal completion of the first (or a subsequent) monolayer, the film thicknesses so obtained are in excellent agreement both with those registered by the thickness monitor and with those deduced from the measured Auger signal ratios using the appropriate sensitivity corrections.<sup>11</sup> AES, LEED, and reflection high-energy electron diffraction (RHEED) were employed to examine the quality of the films. RHEED observations showed that for both overlayer-substrate combinations, monolayer deposition resulted in streaks with the same separation as for the substrate; this indicates that the in-plane spacing

of the atoms in the overlayer is similar to that of the substrate. Good LEED patterns were also observed following monolayer deposition. With continued deposition, however, the RHEED and LEED patterns became increasingly diffuse, but were still discernible after the deposition of  $\sim 3$ – $4$  monolayers.

The polarization of electrons scattered inelastically from a clean Cu(100) surface and from a Cu(100) surface having molybdenum overlayers of thickness 0.5, 1, 2, and 5 monolayers are shown in Fig. 2 as a function of scattered-electron energy. (All the data reported here were recorded under specular conditions with  $\theta_i = \theta_s = 55^\circ$  and are normalized to unit incident electron polarization.) The polarization of electrons scattered inelastically from a clean Mo(110) surface, and a Mo(110) surface with copper overlayers of thickness 1, 2, 3, and 5 monolayers are shown in Fig. 3.

The differences between the polarization versus inelastic energy-loss spectra obtained at clean Cu(100) and Mo(110) surfaces have been discussed previously<sup>2,3</sup> using a simple model which assumes that the detected electrons have each suffered energy loss as a result of a single inelastic electron-hole pair excitation event. The probability that such an inelastic scattering event will result in a spin flip is related to the relative amplitudes for direct and exchange scattering. Molybdenum has a high density of both occupied and unoccupied electronic levels and is therefore expected to exhibit strong inelastic scattering via electron-hole pair excitation. Indeed, the observed polarization-loss feature for Mo(110) shown in Fig. 3 correlates well with the joint density of states available for exchange scattering through electron-hole pair creation.<sup>2</sup> The scattered-electron polarization, however, remains strongly positive showing that, even at the minimum of the polarization-loss feature, non-spin-flip inelastic scattering is dominant. (The data also require that the ratio of spin-flip and non-spin-flip scattering depend on the in-

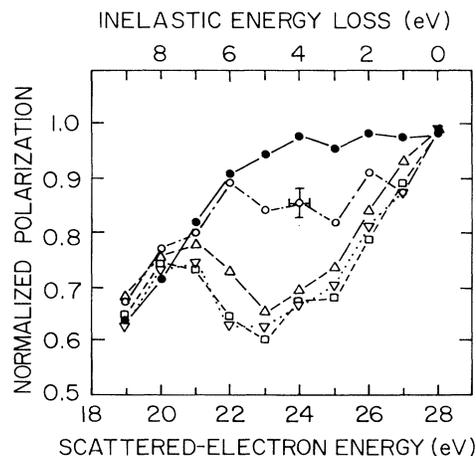


FIG. 2. Polarization of electrons scattered inelastically from a clean Cu(100) surface (●) and following deposition of 0.5 (○), 1 (△), 2 (▽), and 5 (□) monolayers of molybdenum. The data were recorded under specular conditions ( $\theta_i = \theta_s = 55^\circ$ ) with an incident electron energy of 28 eV and are normalized to unit incident electron polarization.

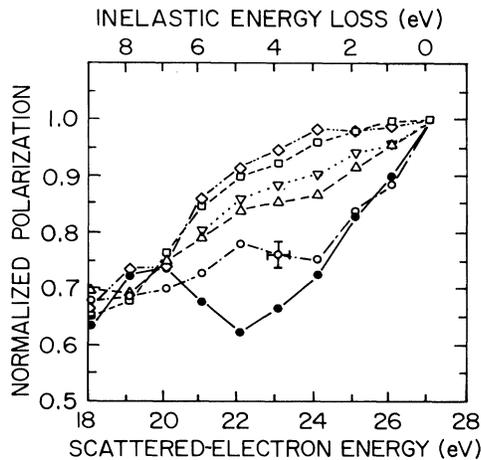


FIG. 3. Polarization of electrons scattered inelastically from a clean Mo(110) surface ( $\bullet$ ) and following deposition of 1 ( $\circ$ ), 2 ( $\Delta$ ), 3 ( $\nabla$ ), and 5 ( $\square$ ) monolayers of copper. Data for clean Cu(100) ( $\diamond$ ) are included for comparison. The data were recorded under specular conditions ( $\theta_i = \theta_s = 55^\circ$ ) with an incident electron energy of 27 eV and are normalized to unit incident electron polarization.

elastic energy loss, but this is not surprising given that both direct and exchange processes contribute to non-spin-flip scattering and that there are interference terms.) Copper has a much lower density of unoccupied states due to the absence of  $d$  holes. As a consequence, for inelastic energy losses  $\lesssim 10$  eV, the joint density of states for electron-hole pair excitation is much smaller than for molybdenum, and the lack of a pronounced polarization-loss feature is not unexpected. Assuming that the detected electrons each undergo a single inelastic scattering event, the probing depths reported here for molybdenum and copper are simply those characteristic of inelastic electron scattering in these materials.

It is notable that the polarization-loss feature observed following deposition of only a single monolayer of molybdenum on Cu(100) approaches in depth and shape that for bulk molybdenum or thick molybdenum films. This indicates that the probing depth for molybdenum must be small,  $\sim 1$  monolayer, and that, as suggested by the LEED and RHEED observations, layer-by-layer growth is occurring, i.e., the copper surface is completely covered following deposition of just a single monolayer of molybdenum. Layer-by-layer growth of molybdenum on Cu(100) is, perhaps, unexpected given that molybdenum has a higher surface free energy ( $\gamma_{\text{Mo}} = 2.2 \text{ J m}^{-2}$ ) than copper ( $\gamma_{\text{Cu}} = 1.6 \text{ J m}^{-2}$ ).<sup>12</sup> The lattice mismatch, however, is small ( $\sim 6\%$ ) and there are other examples of layer-by-layer growth of high-surface-free-energy metals on low-surface-free-energy substrates, at least for the first few monolayers.<sup>13,14</sup> [It has been reported that molybdenum grows epitaxially with (110) orientation on a Cu(111) substrate.<sup>15,16</sup>]

Deposition of copper on Mo(110) leads to a disappearance of the molybdenum polarization-loss feature, but true copperlike behavior is not observed until after deposition of several monolayers. Two explanations for this be-

havior are possible, namely, that the probing depth in copper is large and/or that copper deposition on Mo(110) results in island formation leaving exposed areas of molybdenum that gradually fill in as deposition continues. Other studies, however, have shown that the first layer of copper grows pseudomorphically on Mo(110),<sup>17,18</sup> as was confirmed in the present work by LEED and RHEED observations, and no evidence of island growth has been reported. Figure 3 also shows that the deposition of copper results in a change in the shape of the polarization-loss feature. In particular, the deposition of a single copper monolayer results in a much greater change in the measured polarization at inelastic energy losses of  $\sim 5$  eV than at inelastic energy losses of  $\sim 2$  eV. This effect is difficult to explain in terms of a simple combination of scattering from copper islands and from intervening areas of exposed molybdenum, especially since the energy distributions for electrons scattered inelastically from copper and molybdenum are similar. Thus the data indicate that the probing depth in copper is large,  $\sim 3$  monolayers, and is significantly greater than that for molybdenum. This difference is, however, entirely consistent with differences in the joint densities of states for electron-hole pair excitation. Indeed, if it is assumed that the transition matrix elements coupling occupied and unoccupied levels are independent of energy (and material) and are constant over the Brillouin zone, simple calculations of the joint densities of states for copper and molybdenum predict a difference of a factor of  $\sim 3$  in the probing depths.<sup>2</sup> The data, therefore, suggest that, at least for copper and molybdenum, electron-hole pair excitation is the predominant inelastic electron-scattering mechanism for energy losses of up to  $\sim 10$  eV.

The changes in the shape of the molybdenum polarization-loss feature evident upon copper deposition can be readily explained if the local density of states near the molybdenum/copper interface is described by some linear combination of those appropriate to copper and molybdenum. Given this reasonable conjecture, inelastic spin-flip scattering at the interface might then involve an unoccupied level contributed by the molybdenum substrate but an occupied level contributed by the copper overlayer. (The average density of occupied states for the first few electron volts below the Fermi level is greater for copper than for molybdenum.) Indeed, a simple convolution of the density of unoccupied states for molybdenum with the density of occupied states for a copper surface predicts a polarization-loss feature similar to that observed at intermediate copper coverages. It is also interesting to note that the general shape of the polarization-loss feature observed at a Cu(100) surface with a 0.5-monolayer molybdenum overlayer (see Fig. 2) differs from that for clean Mo(110) but is similar to that for a Mo(110) surface at intermediate copper coverages and this could again be attributed to interface effects. Calculations of the local density of states at a molybdenum/copper interface are underway to test this hypothesis further.<sup>19</sup>

This work is supported by the Division of Materials Sciences, Office of Basic Energy Sciences of the U.S. Department of Energy, and by the Robert A. Welch Foundation.

- <sup>1</sup>*Polarized Electrons in Surface Physics*, edited by R. Feder (World Scientific, Singapore, 1985).
- <sup>2</sup>G. A. Mulhollan, X. Zhang, F. B. Dunning, and G. K. Walters, *Phys. Rev. B* **41**, 8122 (1990).
- <sup>3</sup>X. Zhang, H. Hsu, F. B. Dunning, and G. K. Walters, *J. Vac. Sci. Technol. A* **9**, 1932 (1991).
- <sup>4</sup>J. Kirschner, D. Rebenstorff, and H. Ibach, *Phys. Rev. Lett.* **53**, 698 (1984).
- <sup>5</sup>A. Venus and J. Kirschner, *Phys. Rev. B* **37**, 2199 (1988); J. Kirschner, *Phys. Rev. Lett.* **55**, 973 (1985).
- <sup>6</sup>H. Hopster, R. Raue, and R. Clauberg, *Phys. Rev. Lett.* **53**, 695 (1984).
- <sup>7</sup>D. L. Abraham and H. Hopster, *Phys. Rev. B* **40**, 7054 (1989).
- <sup>8</sup>Y. U. Izerda, D. M. Lind, D. A. Papaconstanpoulos, G. A. Prinz, B. T. Jonker, and J. J. Krebs, *Phys. Rev. Lett.* **61**, 1222 (1988).
- <sup>9</sup>G. A. Mulhollan, X. Zhang, F. B. Dunning, and G. K. Walters, *Phys. Rev. B* **39**, 8715 (1989).
- <sup>10</sup>F. C. Tang, X. Zhang, F. B. Dunning, and G. K. Walters, *Rev. Sci. Instrum.* **59**, 504 (1988); F. B. Dunning, L. G. Gray, J. M. Ratliff, F. C. Tang, X. Zhang, and G. K. Walters, *ibid.* **58**, 1706 (1987).
- <sup>11</sup>*Handbook of Auger Electron Spectroscopy*, 2nd ed., edited by L. E. Davis, N. C. MacDonald, P. W. Palmberg, G. E. Riach, and R. E. Weber (Physical Electronics Industries, Eden Prairie, 1976).
- <sup>12</sup>L. Z. Mezey and J. Giber, *Jpn. J. Appl. Phys.* **11**, 1569 (1982); see also A. R. Miedema, *Z. Metallk.* **69**, 287 (1978).
- <sup>13</sup>R. Germar, W. Dürr, J. W. Krewer, D. Pescia, and W. Gudat, *Appl. Phys. A* **47**, 398 (1988).
- <sup>14</sup>E. Bauer, *Appl. Surf. Sci.* **11/12**, 479 (1982).
- <sup>15</sup>R. Ramirez, A. Rahman, and I. K. Schuller, *Phys. Rev. B* **30**, 6208 (1984).
- <sup>16</sup>E. Bauer and J. H. van der Merwe, *Phys. Rev. B* **33**, 3657 (1986).
- <sup>17</sup>M. Mundschau, E. Bauer, and W. Telieps, *Surf. Sci.* **213**, 381 (1989).
- <sup>18</sup>E. Bauer and H. Poppa, *Thin Solid Films* **121**, 159 (1984).
- <sup>19</sup>A. J. Freeman (private communication).