Origin of Spin-Orbit Splitting for Monolayers of Au and Ag on W(110) and Mo(110)

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Spin-orbit coupling can give rise to spin-split electronic states without a ferromagnet or an external magnetic field. We create large spin-orbit splittings in a Au and Ag monolayer on W(110) and show that the size of the splitting does not depend on the atomic number of the Au or Ag overlayer but of the W substrate. Spin- and angle-resolved photoemission and Fermi-surface scans reveal that the overlayer states acquire spin polarization through spin-dependent overlayer-substrate hybridization.

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Magnetism at interfaces is an important subject within research for future spintronics. In the past it has largely been the magnetic-nonmagnetic interfaces of multilayers that attracted researchers' interest. Between these interfaces, quantum-well states can form that are spin polarized and lead to a long-range oscillatory magnetic coupling, which in turn gives rise to a giant-magnetoresistance effect [1]. In the most recent developments, however, it is the surfaces of heavy metals that allow for the observation of unexpected spin-polarized electronic states [2–9]. These novel effects are not caused by the exchange interaction as for spin-polarized quantum-well states but by the spin-orbit interaction. The findings have been related to the reduced symmetry at the surface because spin-orbit splitting is forbidden in the bulk of centrosymmetric solids due to Kramers degeneracy. The absence of an inversion center at the surface allows for the appearance of nondegenerate pairs of electronic states of opposite spin in the vicinity of the surface. Such surface-derived spin-orbit splitting was observed in photoelectron spectroscopy from the surfaces Au(111) [2,3], W(110) [4,5], Mo(110) [6], Bi(100) [7], and Sb(111) [8]. The choice of these elements enabled the conclusion that the splitting is large for heavy metals Au [2], W (covered by H) [5], Bi [7] and smaller for lighter metals Mo (covered by Li) [6], Sb [8], and too small to be resolved as yet for Ag [9].

The underlying physics of the spin-orbit interaction is usually explained in terms of the Rashba Hamiltonian for spin-orbit coupling induced by an electric field at an interface [10]. For a two-dimensional electron gas the strength of the coupling depends linearly on the confining potential, which opens the possibility of its control by electric fields. It has been argued that within a free-electron model and, in particular, for the reported Au(111) system the expected Rashba splitting is too small and the electric field gradient near the atomic core is essential [9,11]. This would explain the atomic-number dependence. However, the potential step at the surface appears to matter and monovalent adsorbates like Li and other alkali metals have been found to strongly enhance the size of the spin-orbit splitting [6]. For thin films of Mg on W(110), the situation is controversial [12–14]. It had been concluded that due to the large atomic number of the W substrate a large spin-orbit splitting can be induced in Mg thin films similar to quantum-well states that become spin polarized due to the exchange interaction in the substrate [12]. This would constitute an important step towards the spin transistor. However, we have recently shown that this large Mg splitting remains unchanged when W is replaced by Mo [14]. We concluded that the observed splitting is not due to spin-orbit coupling but to the interaction with surface states of W, which had been neglected in previous work [12,13].

The influence of the core potential is also illustrated by the increased splitting for Ag(111), which was found when Ag was alloyed with Au, and it was concluded that the spin-orbit splitting is proportional to the number of heavy atoms probed by the surface-state wave function [15]. A splitting also appeared in Ag when it was grown as epitaxial film on Au(111), thus supporting this conclusion further.

Starting from this idea, we pose the question of how important for the spin-orbit splitting is the number of heavy atoms probed by the surface-state wave function as compared to the potential gradient at the surface or interface. In the present Letter we employ Au and Ag as well-defined noble-metal monolayers on W and Mo to study the role of the interface for the spin-orbit splitting. We find that large splittings are created for 1 monolayer (ML) Au/W(110) but the splitting neither depends on the atomic number of the overlayer nor does the Au cause a particular change in the electric field gradient.

$E(k)$ dispersion relations have been measured from samples prepared as described earlier [16] by angle-resolved photoemission at the Russian-German beam line at BESSY with p-polarized light and a hemispherical electron energy analyzer. The Fermi-surface measure-

ments have been done at the TGM4 beam line with a second-generation toroidal electron energy analyzer by means of azimuthal scans [17]. Spin- and angle-resolved spectra were measured at the UE112/PGM-LE beam line with a hemispherical analyzer and a Rice University Mott polarimeter operated at 26 kV.

Figure 1 shows angle-resolved photoemission spectra of W(110) covered with 1 ML of (a) Au and (b) Ag. From top to bottom the surface-projected electron wave vector varies along the $\bar{S}$-$\bar{\Gamma}$-$\bar{S}$ direction of the surface Brillouin zone with the normal-emission spectrum at $\bar{\Gamma}$ highlighted by bold linewidth. (Similar results are found along $\bar{\Gamma}$-$\bar{H}$.) We observe two prominent dispersing features marked as 1 and 2, which do not exist for clean W(110). Figure 1(c) shows comparable data for 1 ML Au/Mo(110) where the same dispersion appears but no splitting is seen (marked 1 + 2). Data for 1 ML Ag/Mo(110) (not shown) are similar. Besides features 1 and 2 we note that around normal emission all systems show quantum-well-state peaks characteristic of 1 ML Au (3.7 and 3.1 eV) and Ag (4.15 and 4.6 eV), respectively. This assignment has been established [16], and it enables precise control of the film thickness with an accuracy as high as ± 0.1 ML.

Figure 2 shows $E(k)$ dispersions extracted from such data in a representation of photoemission intensity vs emission angle and as extracted data points vs the surface-projected electron wave vector $\mathbf{k}_{\parallel}$. In these figures,

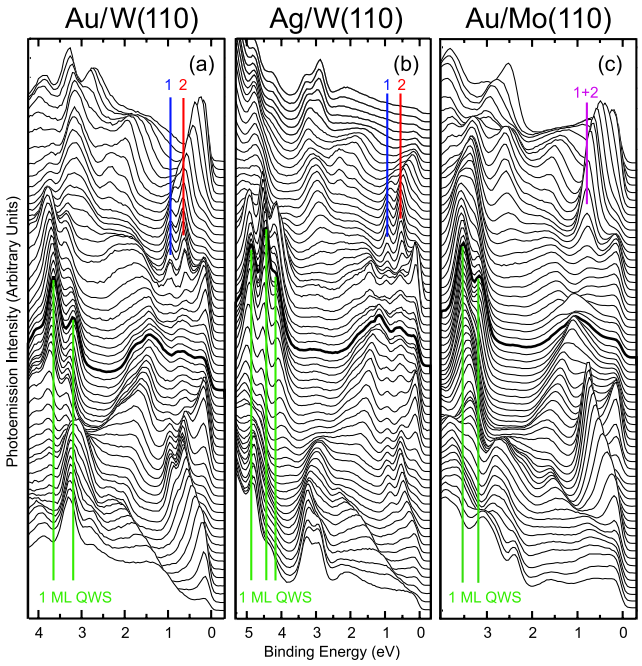

FIG. 1 (color online). Angle-resolved photoemission spectra along the $\overline{\Gamma S}$ direction for (a) 1 ML of Au/W(110) and (b) Ag/W(110) ($h\nu = 65$ eV). Spin-orbit split states and quantum-well states (QWS) for 1 ML are marked by lines. The spin-orbit splitting is of similar size for Au and Ag but vanishes for (c) Au/Mo(110).

blue hatching marks (110)-surface-projected bulk states of W and Mo [6,12]. Figure 2 shows that (i) for both Au and Ag monolayers, the split bands 1 and 2 are most pronounced when inside of this bulk band gap, (ii) their dispersions $E(k)$ do not depend on the photon energy (symbol

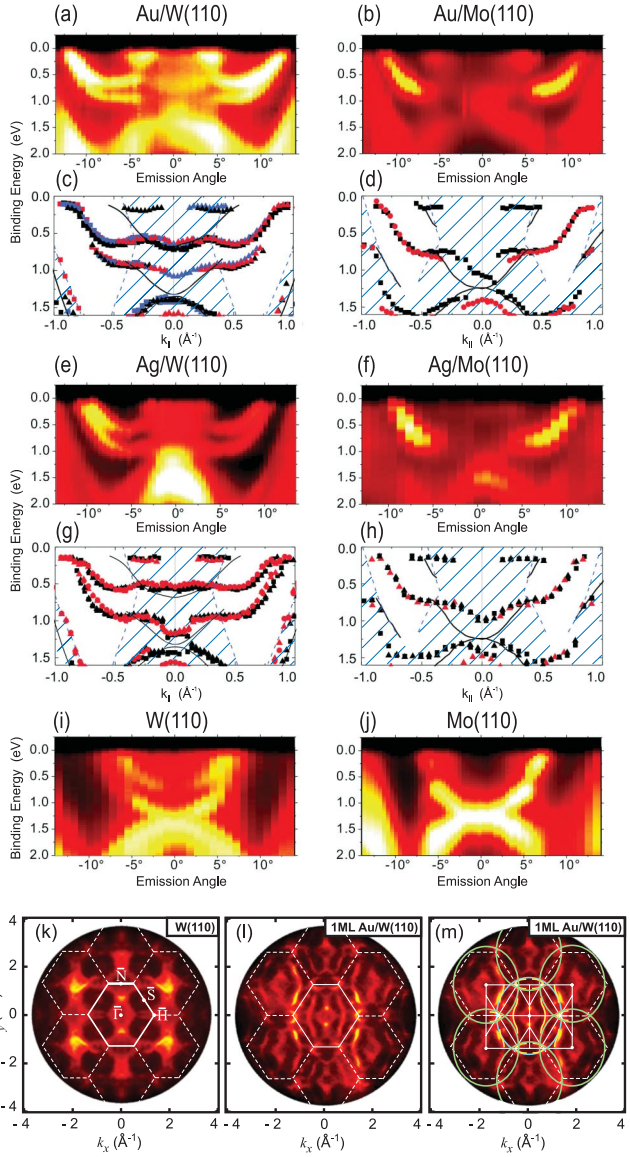

FIG. 2 (color). $E(k)$ dispersion relations along $\overline{\Gamma S}$ from photoemission spectra. (a) 1 ML Au on W(110) and (b) on Mo(110), $h\nu = 65$ eV; (e) 1 ML Ag on W(110) and (f) on Mo(110), $h\nu = 80$ eV. Corresponding $E(\mathbf{k}_{\parallel})$ dispersions measured at $h\nu = 62$ eV (blue), 65 eV (black), and 80 eV (red). $E(\mathbf{k}_{\parallel})$ data of (i) pure W(110) and (j) Mo(110), $h\nu = 65$ eV, are indicated by black lines (c),(d),(g),(h). The new features are inside of a gap where bulk states (blue hatching) are forbidden. The Fermi surface of (k) clean W(110) changes dramatically after deposition of (l) 1 ML Au, $h\nu = 62.5$ eV. (m) Correspondence between features in the first, second, and third surface Brillouin zones is consistent with an almost circular Fermi surface outside of the first zone (see text).

color) inside of the gap, which clearly indicates their two-dimensionality, (iii) the splitting between 1 and 2 has a similar value for Au/W(110) and Ag/W(110). This is counterintuitive in view of the huge difference between atomic numbers of $_{79}$Au and $_{47}$Ag and measured spin-orbit splittings of Au(111) and Ag(111) surface states and may indicate that the split dispersion branches are W derived. (iv) The splitting amounts to 0.35 eV at $\mathbf{k}_{\parallel} = 0.5$ Å^{-1} and is k dependent. (v) For Mo-derived systems the splitting is absent.

In order to assess the overlayer or substrate origin of the split features, we have studied the coverage dependence at 8° off-normal emission and 80 eV photon energy in Fig. 3. Again, the observation of quantum-well peaks (for 1 and 2 ML) guarantees layer growth and thickness calibration. We see in Figs. 3(c) and 3(d) that the intensities of the split peaks grow from zero simultaneously with that of the 1-ML-quantum-well state and steadily decreases when the 2-ML-quantum-well state forms. The feature is, therefore, overlayer derived. The splitting itself in Figs. 3(a) and 3(b) does not change significantly with thickness. This contrasts the findings for the system Li/W(110) where the spin-orbit splitting markedly increases between 0.5 and 1 ML [6].

The overlayer-derived nature is corroborated by the effect on the Fermi surface [Figs. 2(k) and 2(l)]. Apparently, the Fermi surface of W in Fig. 2(k) undergoes a complete rearrangement to the extent that the most prominent features in Fig. 2(l), namely, the ones observed along $\overline{\Gamma S}$ and $\overline{\Gamma H}$ in Figs. 1–4, are states induced by the Au monolayer. Interestingly, the periodicity of the reciprocal

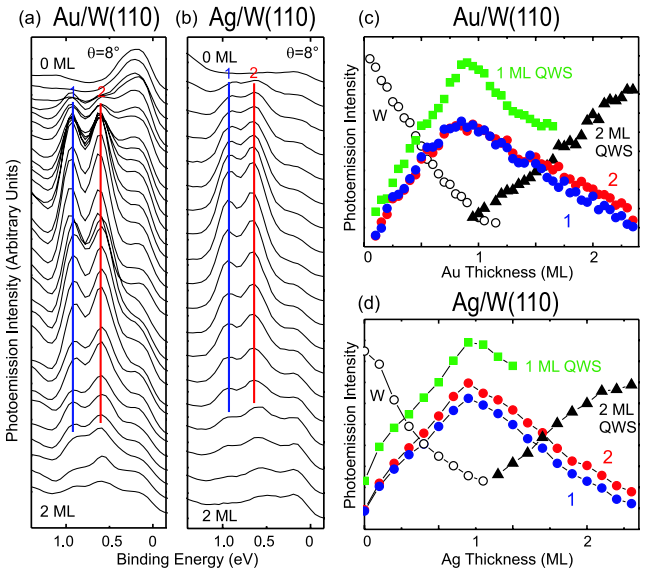

FIG. 3 (color online). Coverage dependence of photoemission spectra for (a) 0–2 ML Au and (b) Ag on W(110) [$h\nu = 80$ eV, 8° off-normal emission along (a) $\overline{\Gamma H}$ and (b) $\overline{\Gamma S}$]. Spin-orbit split states are marked, and (c),(d) their intensities are compared to those of a W-derived state and quantum-well states for 1 and 2 ML as a function of coverage.

lattice of bcc (110) of W is fully maintained. This confirms the epitaxial growth of the Au monolayer in registry with W(110) [18,19]. For 2 ML Au (not shown) the Fermi surface already shows a threefold symmetry representative of Au(111). This change agrees well with the observation in Figs. 2 and 3 that the new spin-orbit split states are a peculiar property of the thickness 1 ML.

In Fig. 2(m) we show how all features observed (yellow lines), including the prominent sickle-shaped sections, can be explained based on a (slightly elongated) free-electron Fermi surface. This is a strong proof of the Au-derived nature of the band in question. Note that thereby all features are assigned. No other feature appears that could be assigned to the Au $6sp$ states. Conversely, an overall circular Fermi surface cannot originate from the $5d$ states that form the W valence band. The idealized Fermi surface of Au of Fig. 2(m) (green) leads to a hole pocket at $\bar{\Gamma}$ when placed onto the reciprocal lattice of W(110) because this Fermi surface is situated completely outside of the first surface Brillouin zone of W(110). This hole pocket corresponds to a negative slope of $E(k)$ (effective mass $m^* < 0$) in the first Brillouin zone. This is the expectation for a noninteracting Au overlayer. Instead, the slope in Fig. 2(a) is positive, which consequently must be due to strong interaction with the substrate, facilitated by the perfect epitaxy. In Fig. 4 the spin polarization is measured in the film plane approximately perpendicular to $\mathbf{k}_{\parallel}$, and the resulting photoemission spectra for the two spin directions show that the splitting of Fig. 1 is indeed a spin-orbit splitting according to the Rashba model, in particular, because the orientation of the spin reverses with the sign of the off-normal-emission angle. The splitting amounts to 0.3–0.4 eV. For a noninteracting Au overlayer, the spin-orbit splitting would have to increase linearly with increasing $\mathbf{k}_{\parallel}$, according to the Rashba model. Instead, this state shows a splitting *decreasing* with increasing $\mathbf{k}_{\parallel}$. It does not vanish for $\mathbf{k}_{\parallel} \rightarrow 0$ but, instead, the intensity vanishes. Exactly this behavior is seen for the bare W(110) [Fig. 2(i)] as well as for H/W(110) [4] and not for Mo(110) [Fig. 2(j)]. We actually find that clean W(110) shows the same dispersions near the band gap as H/W(110) does (not shown), so we can assign the two prominent W dispersions in Fig. 2(i) to spin-orbit split peaks corresponding to the spin-resolved measurements of H/W(110) at 0.5 and 1.0 eV at ~0.3 Å^{-1} along $\overline{\Gamma S}$ [5]. This means for the present results that the Au-derived band in Fig. 2(a) hybridizes with a band that is already spin-orbit split for pure W. This hybridization is apparently spin dependent so that the Au- or Ag-derived band inherits the spin-orbit splitting. Vanishing splitting in Mo leads to vanishing splitting in Au and Ag.

A remaining question is the one for the potential gradient at the surface or interface. It is tempting to generally assign the spin-orbit splitting to the interface dipole, which is pronounced for Li/W. The present results where Au

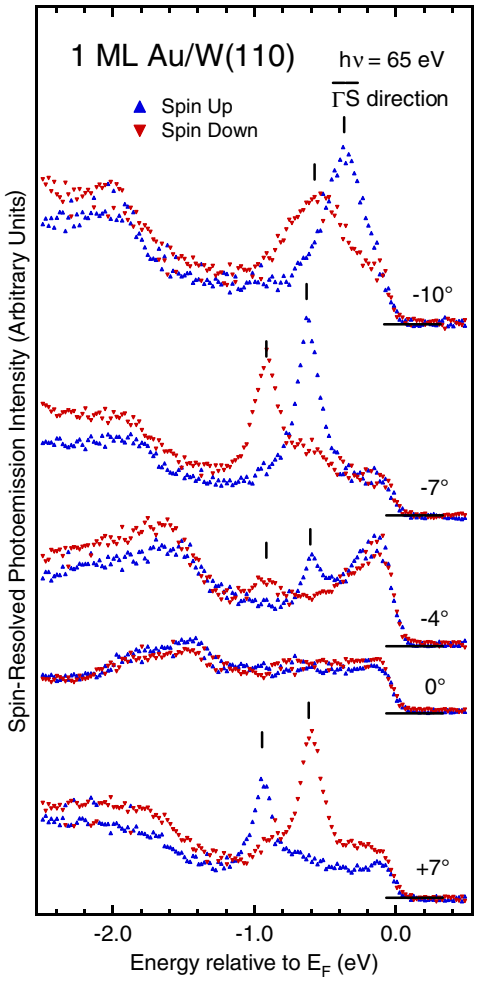

FIG. 4 (color online). Spin-resolved photoemission for various emission angles along $\overline{\Gamma S}$ ($h\nu = 65$ eV) confirming the interpretation as spin-orbit splitting.

induces changes as strong or even stronger than for Li prove that a strong dipole is not essential for creating spin-orbit split adsorbate-induced electronic states on W since electronegativities show clearly that practically no dipole forms at interfaces such as Au/W. It is interesting in this context that also in the field of quantum-well states the first photoemission observations were made on alkali-metal films. The spectral features had originally been linked to the large dipole moment and were explained by a charge transfer effect [20] before the correct interpretation was given [21]. We suggest that the Fermi wave vector with magnitude k_F of the adsorbate material determines the properties of the two-dimensional Fermi surface of the various monolayer systems. The $E(k)$ dispersions of Au/W(110) are similar but somewhat shifted as compared to the full monolayer Li/W(110) [6], possibly because k_F of Au (1.2 Å^{-1}) is similar to k_F of Li (1.1 Å^{-1}).

In conclusion, we studied the behavior of new two-dimensional states on W(110) and Mo(110) induced by a Au and Ag monolayer. A spin-orbit splitting can be resolved. Comparison between Au, Ag, W, and Mo shows that the atomic number of the overlayer is of little relevance, which is different from the situation encountered with surface states on Au, Ag(111), where the number of heavy atoms probed by the wave function was found essential for the splitting. The present results for the noble-metal passivated W(110) show that a large interface dipole or charge transfer as with alkali/W(110) are not a prerequisite for observation of a large spin-orbit splitting. The states are identified as Au derived by their thickness dependence and Fermi surface but the band dispersion and behavior of the spin-orbit splitting with $\mathbf{k}_{\|}$ show that spin-dependent hybridization with substrate states enables them to acquire spin polarization.

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